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Random Sequential Addition: A Distribution Function Approach

Gilles Tarjus,[1] Pierre Schaaf,[2] and Julian Talbot[3]

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Random sequential addition (RSA) of hard objects is an irreversible process defined by three rules: objects are introduced on a surface (or a d-dimensional volume) randomly and sequentially, two objects cannot overlap, and, once inserted, an object is clamped in its position. The configurations generated by an RSA can be characterized, in the macroscopic limit, by a unique set of distribution functions and a density. We show that these "nonequilibrium" RSA configurations can be described in a manner which, in many respects, parallels the usual statistical mechanical treatment of equilibrium configurations: Kirkwood–Salsburg–like hierarchies for the distribution functions, zero-separation theorems, diagrammatic expansions, and approximate equations for the pair distribution function. Approximate descriptions valid for low to intermediate densities can be combined with exact results already derived for higher densities close to the jamming limit of the process. Similarities and differences between the equilibrium and the RSAconfigurations are emphasized. Finally, the potential application of RSA processes to the study of glassy phases is discussed.

KEY WORDS: Random sequential addition; hard-core particles; distribution functions; nonequilibrium configurations; Kirkwood–Salsburg-like equation.

1. INTRODUCTION

A variety of physical, chemical, biological, and ecological problems can be modeled as random sequential additions (RSA) of objects.[1–12] An RSA process is defined by the following three rules: (i) objects are adsorbed on a surface (or more generally inserted in a d-dimensional volume) randomly

[1] Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie, 75252 Paris Cédex 05, France.
[2] Institut Charles Sadron (CRM-EAHP), CNRS-ULP, 67083 Strasbourg Cédex, France.
[3] School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907.

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and sequentially, (ii) two objects cannot overlap, and (iii) once inserted, an object is clamped in its position, that is, it can neither move on the surface nor be removed. The latter rule implies that RSA is an irreversible process. The properties of the configurations of objects produced by RSA are thus different from those of equilibrium systems which can be described by means of usual statistical mechanics.[13] Both RSA and equilibrium may be viewed as limiting cases of real adsorption or addition processes: in the "equilibrium" case, the assembly of objects relaxes rapidly to equilibrium between two successive additions, whereas in RSA it remains immobile.[13] Time scales are thus crucial for determining the applicability of the RSA model. The RSA is well suited, for instance, for describing the adsorption of latexes or proteins on solid surfaces under some conditions. Very often, activation energies are much higher for the desorption process than for the adsorption process, and the adsorbed particles stick on the surface and diffuse very slowly, so that on the time scale of an experiment desorption and diffusion are negligible.[6,7,12]

The RSA model has been widely studied analytically as well as by computer simulations. Most of the studies considered lattice models,[1–3,11,13,15–20] but instead we focus here on a continuous description of space: the systems of adsorbed objects represent the RSA counterparts of the familiar hard-disk, hard-sphere, etc., fluids at equilibrium. The results so far obtained for such processes may be summarized as follows. An RSA process asymptotically reaches a jamming limit, in which no more objects can be introduced. The corresponding saturation density is known exactly in one dimension[21] and is derived from computer simulations in two and three dimensions.[4,6,7,22–26] Some features of the asymptotic approach to the jamming limit can be determined analytically.[22,26–28] The one-dimensional case, known as the parking problem, is exactly solvable,[3,13] and, in two dimensions, an approximate description is available for the short-time/low-density regime.[29] Additional insight is provided by several computer simulation studies[7,9,22,29] and, in particular, by a geometrical description of two-dimensional RSA configurations close to the jamming limit by Hinrichsen *et al.*[22] But still no systematic approach to RSA processes associated with a continuous description of space has been yet proposed.

The main goal of this paper is to provide a systematic description of such RSA processes and of the configurations of objects created by RSA. We have noted that RSA and equilibrium correspond to two limiting, and in a way opposite, situations. Parallels and differences between the two situations were first emphasized by Widom,[13] and we try here to pursue the comparison as far as possible. Some of the most powerful tools of equilibrium statistical mechanics cannot be used in the study of RSA configura-

tions. However, simple probabilistic and geometric arguments apply in the context of nonequilibrium as well as equilibrium situations.[30,31] Working along these lines, we show that RSA configurations can be described exactly by means of a hierarchy of equations for the distribution functions which is *analogous to the Kirkwood–Salsburg (KS) hierarchy* for systems at equilibrium.[32] Some exact results, denoted *zero-separation theorems*, are derived.

The KS-like hierarchy is not exactly solvable in general and approximate solutions are needed. Our approach rests on the observation that the kinetics of an RSA process can be roughly divided into two regimes: an asymptotic regime associated with the slow approach to the jamming limit and an "initial" regime corresponding to low to intermediate densities of adsorbed objects. Since analytic results are already available for the asymptotic/high-density regime, we focus on the initial regime. We expect that a good description of the RSA process over the entire density range can be attained by combining the exact results for high densities close to the jamming limit with approximate solutions obtained for low to intermediate densities. Here we develop treatments capable of providing approximate solutions: they consist in *density and diagrammatic expansions*, as well as *an approximate (Percus–Yevick-like) equation for the pair distribution function.* Parallelism with equilibrium statistical mechanics is striking and, at each step of the treatment, we note differences and similarities between equilibrium and RSA results. Finally, we discuss the potential application of RSA processes to the study of (nonequilibrium) glassy states.

2. DERIVATION OF A KS-LIKE HIERARCHY

In this section, we derive an exact hierarchy of equations characterizing the RSA of hard objects with a spherical symmetry (hard disks, hard spheres, etc.). We use the language of two-dimensional systems, namely adsorption of hard disks of diameter σ on a flat uniform surface, which we find easier to visualize, but the results are directly applicable to any dimension. The kinetics of the RSA is studied as usual by starting at time $t=0$ with an empty surface placed in contact with a "bulk phase" of particles, and by assuming that the irreversible adsorption of a particle on an empty surface, i.e., in absence of excluded surface effects, is characterized by a rate constant k_a (note that in a computer simulation, $k_a t$ is related to the number of attempts made to add disks on the surface and is thus discretized).

An RSA process produces random disordered configurations,[13] and in the macroscopic limit where both the number of adsorbed disks and the area of the surface become infinite while the number density ρ stays finite,

all generated configurations of adsorbed objects are characterized, at any given time t, by a unique density $\rho(t)$ and a unique set of distribution functions $\{g_n(1,..., n; t)\}$, where 1,..., n is a short-hand notation for the position vectors $\mathbf{r}_1,..., \mathbf{r}_n$.[4] Moreover, the system formed by the adsorbed objects is macroscopically uniform (homogeneous and isotropic).

From a microscopic point of view, the kinetics of the RSA process is not only represented by the time evolution of the density $\rho(t)$, but more generally by the time evolution of the typical configurations. We thus look for a hierarchy of equations to be satisfied by the density and the various distribution functions.

As previously shown,[29] the increase with time of the density of adsorbed disks is governed by the following equation:

$$\frac{d}{dt}\rho(t) = k_a \Phi(t) \tag{1}$$

where $\Phi(t)$ is the fraction of the total surface which at time t is available for the center of a new adsorbing disk. Because of the macroscopic uniformity of the system, Φ also represents the probability that around any position $\mathbf{r}_1$ there is a region with a diameter of at least 2σ which is free from any center of preadsorbed disks. It is given by

$$\Phi(t) \equiv \Phi(1; t) = 1 + \sum_{s=1}^{\infty} \frac{\rho(t)^s}{s!} \int \cdots \int d2 \cdots d(s+1)\, f_{12} \cdots f_{1(s+1)} \times g_s(2,..., (s+1); t) \tag{2}$$

where each integral is taken over the whole surface and $f_{ij} \equiv f(|\mathbf{r}_i - \mathbf{r}_j|)$ is a Mayer f-function for hard bodies and is thus equal to (-1) when $|\mathbf{r}_i - \mathbf{r}_j| < \sigma$ and to 0 otherwise. Equations (1) and (2) were derived by means of geometric and probabilistic arguments which we now apply to the time evolution of the distribution functions. Instead of repeating the

[4] A heuristic argument in favor of the unicity of the density and set of distribution functions for RSA configurations considered at a given time t is obtained by applying the well-known device used in equilibrium statistical mechanics to show that the relative fluctuations of all physical additive quantities decrease as the inverse of the square root of the volume (or surface in $2d$) of the system (e.g., ref. 33; see also, in the context of a nonequilibrium situation, ref. 34): a very large but finite surface is divided into a large number of subsystems, the size of which is much larger than any typical characteristic length of the problem. Edge and interface effects can be neglected so that, at a given time t, the configurations of objects in each subsystem can be considered as produced by independent RSA processes. Use of the central limit theorem then ensures that the fluctuations of the quantities like the density $\rho(t)$ (and all particle densities for uniform systems) go as the inverse of the square root of the total area of the surface.

proof of Eqs. (1) and (2), which can be found elsewhere,[29,30,35] we detail the steps for deriving a similar equation for the pair distribution function. $\rho(t)^2 g_2(1, 2; t)$ is the two-particle density characterizing the configuration at time t: $\rho(t)^2 g_2(1, 2; t)\, d\mathbf{r}_1\, d\mathbf{r}_2$ is thus equal to the probability that the center of one (unspecified) particle is in $d\mathbf{r}_1$ around $\mathbf{r}_1$ and the center of one (unspecified) particle is in $d\mathbf{r}_2$ around $\mathbf{r}_2$. Due to the irreversibility of the RSA process, the two-particle density, whatever the positions $\mathbf{r}_1$ and $\mathbf{r}_2$ are, can only increase with time. Creation of new pairs between times t and $t+dt$ is achieved by adsorption of a disk at point $\mathbf{r}_2$ conditional on the presence of a preadsorbed disk at point $\mathbf{r}_1$ or adsorption of a disk at point $\mathbf{r}_1$ conditional on the presence of an already adsorbed disk at point $\mathbf{r}_2$. The rate at which the two-particle density increases may then be written as

$$\frac{\partial}{\partial t}\rho(t)^2 g_2(1, 2; t) = k_a[\Phi(1\,|\,2; t) + \Phi(2\,|\,1; t)] \tag{3}$$

where $\Phi(i\,|\,j; t)$ is the density of disks centered at point $\mathbf{r}_i$ given that space is still available at the point $\mathbf{r}_j$ for the center of a new adsorbing disk. Because of the macroscopic properties of the system (isotropy and homogeneity), $\Phi(i|j; t)$ is actually a function of the distance $|\mathbf{r}_i - \mathbf{r}_j|$ only and is invariant under the permutation $i \Leftrightarrow j$. In the limit of vanishing densities ($t \to 0, \rho \to 0$), $\Phi(i|j; t)$ is simply equal to the average density $\rho(t)$ if $|\mathbf{r}_i - \mathbf{r}_j| > \sigma$ and is equal to zero otherwise. However, when the density increases, one has to take into account the fact that the environment of the disk centered at $\mathbf{r}_i$ is already crowded by other disks and that adsorption of a new disk at $\mathbf{r}_j$ may be precluded by the presence of one, two, or more disks. These latter disks are those whose centers are located within a circle of diameter 2σ around $\mathbf{r}_j$: cf. Fig. 1. Then $\Phi(i|j; t)$ can be expressed as

$$\begin{aligned} \Phi(i\,|\,j; t) &= \rho(t) - \sum_{r=1}^{\infty} \rho_r(i\,|\,j; t), \qquad |\mathbf{r}_i - \mathbf{r}_j| > \sigma \\ &= 0, \qquad\qquad\qquad\qquad\quad |\mathbf{r}_i - \mathbf{r}_j| < \sigma \end{aligned} \tag{4}$$

where $\rho_r(i|j; t)$ is the density of particles centered at $\mathbf{r}_i$ given that the centers of *exactly* r disks are located within the circle of diameter 2σ around $\mathbf{r}_j$. Using a procedure outlined by Reiss *et al.*[35] and Torquato and Stell,[36] we can rewrite Eq. (4) as

$$\begin{aligned} \Phi(i\,|\,j; t) &= \rho(t) - [\rho_1(i\,|\,j; t) + 2\rho_2(i\,|\,j; t) + 3\rho_3(i\,|\,j; t) + \cdots] \\ &\quad + [\rho_2(i\,|\,j; t) + 3\rho_3(i\,|\,j; t) + 6\rho_4(i\,|\,j; t) + \cdots] - \cdots \\ &= \rho(t) + \sum_{s=1}^{\infty} (-1)^s \sum_{r=s}^{\infty} C_r^s \rho_r(i\,|\,j; t), \qquad |\mathbf{r}_i - \mathbf{r}_j| > \sigma \end{aligned}$$

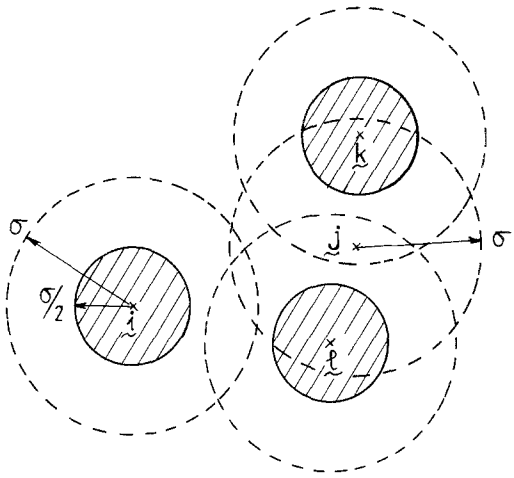


Fig. 1. A disk of diameter σ has an associated exclusion disk of diameter 2σ from which the centers of other disks are excluded. The presence of the two disks centered at k and l thus prevents the adsorption of a new disk whose center would be at j.

where C_r^s denotes a binomial coefficient. Equation (5) is easily interpretable by noting that $[\rho_1(i|j;t)+2\rho_2(i|j;t)+3\rho_3(i|j;t)+\cdots]\,d\mathbf{r}_i$ is the *average* number of pairs such that the center of one particle is in $d\mathbf{r}_i$ around $\mathbf{r}_i$, while the center of the other one lies within 2σ of $\mathbf{r}_j$, and that, more generally,

$$\left[\sum_{r=s}^{\infty} C_r^s \rho_r(i|j;t)\right] d\mathbf{r}_i$$

is the *average* number of $(s+1)$-tuplets such that the center of one particle is in $d\mathbf{r}_i$ around $\mathbf{r}_i$ and the centers of s particles lie within 2σ of $\mathbf{r}_i$. Equation (5) proceeds by successive corrections, providing alternately upper and lower bounds to $\Phi(i|j;t)$. Taking now into account the definitions of the Mayer f-functions and the distribution functions, we obtain an expression for the average number of $(s+1)$-tuplets which leads to

$$\Phi(i|j;t) = (1+f_{ij})\left\{\rho(t) + \sum_{s=1}^{\infty} \frac{\rho(t)^{s+1}}{s!} \int \cdots \right.$$
$$\left. \times \int dk_1 \cdots dk_s\, f_{jk_1} \cdots f_{jk_3}\, g_{s+1}(i, k_1, \ldots, k_s; t)\right\} \qquad (6)$$

where $(1+f_{ij})$ is a geometric factor which ensures that $\Phi(i|j;t)$ is zero when $|\mathbf{r}_i - \mathbf{r}_j| < \sigma$. Notice that due to the fact that Mayer f-functions are

negative, the series in Eq. (6) is alternate, as it is in Eq. (5). Combination of Eq. (6) and Eq. (3) provides the expression we seek for the pair distribution function.

The preceding method can be easily applied to the n-particle distribution function. With $\rho(t)^n\, g_n(1,..., n; t)\, d\mathbf{r}_1 \cdots d\mathbf{r}_n$ the probability that the center of one (unspecified) particle is in $d\mathbf{r}_1$ around $\mathbf{r}_1$,..., and the center of one (unspecified) particle is in $d\mathbf{r}_n$ around $\mathbf{r}_n$, the rate at which the n-particle density $\rho(t)^n\, g_n(1,..., n; t)$ increases with time is given by

$$\frac{\partial}{\partial t}\rho(t)^n\, g_n(1,..., n; t) = k_a \sum_{i=1}^{n} \Phi(1,..., i-1, i+1,..., n \mid i; t) \tag{7}$$

where $\Phi(1,..., i-1, i+1,..., n \mid i; t)$ is the density of $(n-1)$-tuplets centered at $\mathbf{r}_1,..., \mathbf{r}_{i-1}, \mathbf{r}_{i+1},..., \mathbf{r}_n$, such that space is still available at the position $\mathbf{r}_i$ for the center of an nth disk. A straightforward generalization of Eq. (4)–(6) leads to

$$\begin{aligned}
&\Phi(1,..., i-1,..., n \mid i; t) \\
&\quad = \prod_{\substack{j=1 \\ j\neq i}}^{n} (1+f_{ij}) \sum_{s=0}^{\infty} \frac{\rho(t)^{n+s-1}}{s!} \int \cdots \int d(n+1) \cdots \\
&\qquad \times d(n+s)\, f_{i(n+1)} \cdots f_{i(n+s)}\, g_{n+s-1} \\
&\qquad \times (1,..., i-1, i+1,..., n, n+1,..., n+s; t)
\end{aligned} \tag{8}$$

where $\prod_{j=1, j\neq i}^{n} (1+f_{ij})$ is a simple geometric factor, equal either to 1 or 0, which ensures that the nth disk introduced at r_i will not overlap with the $(n-1)$ disks already adsorbed. In writing Eq. (8), we chose the convention that the $s=0$ term reduces to $\rho(t)^{n-1}\, g_{n-1}(1,..., i-1, i+1,..., n; t)$.

The preceding equations—Eqs. (1), (2); (3), (6); and (7), (8),—form a hierarchy and provide a full microscopic description of the kinetics of the RSA process. This hierarchy derived for hard isotropic objects can be used to describe the RSA of hard anisotropic objects: the arguments i, j,..., of all functions refer then to the positions and orientations $(\mathbf{r}_i, \Omega_i)$, $(\mathbf{r}_j, \Omega_j)$,..., and, accordingly, the integrations are taken over positions and orientations.

Connection with the statistical mechanical description of equilibrium fluids is made by taking advantage of the one-to-one mapping which exists for the RSA process between the time, $t \in [0, +\infty[$, and the density of adsorbed particles, $\rho \in [0, \rho_s[$, where ρ_s is the saturation density at the jamming limit. Using then the identity

$$\frac{\partial}{\partial t} = k_a \Phi(\rho) \frac{\partial}{\partial \rho} \tag{9}$$

which is a direct consequence of Eq. (1), together with defining new functions $S_n(1,..., n; \rho)$ as

$$S_1(1; \rho) = S_1(\rho) = \Phi(\rho) \tag{10a}$$

$$\rho^{n-1} S_n(1,..., n; \rho) = \frac{1}{n} \sum_{i=1}^{n} \Phi(1,..., i-1, i+1,..., n \mid i; \rho) \tag{10b}$$

where the various Φ are given by Eqs. (2), (3), and (8), we derive from Eqs. (7) and (8) the following hierarchy of equations:

$$\frac{1}{n\rho^{n-1}} \frac{\partial}{\partial \rho} [\rho^n g_n(1,..., n; \rho)] = \frac{S_n(1,..., n; \rho)}{S_1(\rho)}, \qquad n \geqslant 1 \tag{11}$$

with

$$S_n(1,..., n; \rho) = \frac{1}{n} \sum_{i=1}^{n} \prod_{\substack{j=1 \\ j \neq i}}^{n} (1 + f_{ij}) \left\{ \sum_{s=0}^{\infty} \frac{\rho^s}{s!} \int \cdots \int d(n+1) \cdots d(n+s) f_{i(n+1)} \cdots \right.$$

$$\left. \times f_{i(n+s)} g_{n+s-1}(1,..., i-1, i+1,..., n, n+1,..., n+s; \rho) \right\} \tag{12}$$

Because of geometric constraints on the packing of impenetrable objects, the sum over s present in the right-hand-side of Eq. (12) can be actually restricted to a small finite number of terms: 2 in one dimension, 6 in two dimensions, 12 in three dimensions, etc.

By analogy with the equilibrium situation, we call Eqs. (11), (12) the *Kirkwood–Salsburg-like hierarchy for the RSA distribution functions.* Justification for this terminology is found by noting that the Kirkwood–Salsburg (KS) hierarchy for an equilibrium ensemble[32] can be written as

$$g_n^{eq}(1,..., n; \rho) = \frac{S_n^{eq}(1,..., n; \rho)}{S_1^{eq}(\rho)}, \qquad n \geqslant 1 \tag{13}$$

when using the well-known relation between the thermodynamic activity z and $S_1^{eq}(\rho)$:

$$S_1^{eq}(\rho) = \Phi^{eq}(\rho) = \rho / z \tag{14}$$

$S_n^{eq}(1,..., n; \rho)$ is expressed in terms of the distribution functions g_{n+s-1}^{eq}, $s \geqslant 0$, by an equation formally identical to Eq. (12). For an equilibrium

ensemble, all the n terms of the sum over i are identical, so that Eq. (12) may be simply replaced by

$$S_n^{\mathrm{eq}}(1,\ldots,n;\rho)=\prod_{j=2}^{n}(1+f_{1j})\sum_{s=0}^{\infty}\frac{\rho^s}{s!}\int\cdots\int d(n+1)\cdots d(n+s)$$
$$\times f_{1(n+1)}\cdots f_{1(n+s)}g_{n+s-1}^{\mathrm{eq}}(2,\ldots,n+s;\rho) \tag{15}$$

Such a simplification is impossible in the RSA case: the distribution function $g_n(1,\ldots,n)$ is of course invariant under any permutation of $1,\ldots,n$; however, because of the irreversibility of the RSA process, the order in which particles are adsorbed on the surface must be taken into account explicitly.

According to Stell's language,[30] Eqs. (11) and (13) provide two examples of different "closure relations" for KS-like hierarchies. The specific irreversible kinetics of the RSA process leads to an additional term, namely

$$\frac{\rho}{n}\frac{\partial}{\partial\rho}g_n(1,\ldots,n;\rho)$$

in the left-hand-side of the "closure relation."

Finally, connection can be made between the preceding results and the various hierarchical rate equations used in the context of lattice models. For instance, in studying distributions of adatoms resulting from dissociative adsorption of a diatomic gas on a two-dimensional lattice, Hoffman derived a hierarchy of equations for the distribution functions which is analogous to what we have called the Kirkwood–Salsburg-like hierarchy.[15] Interestingly, Hoffman's derivation of the hierarchy was based on a method quite different from that used in the present paper. The adsorption process on the lattice was assumed to be activated and equations for the distribution functions were obtained from a kinetic equation written in the framework of the grand-ensemble theory. More recently, Evans[37] mentioned that the hierarchical rate equations he had previously written for lattices[11,16,17] could apply to the continuum case in order to give the first terms of the density expansion of $\Phi(\rho)\equiv S_1(\rho)$: in such a case, the hierarchies directly provide equations for the successive time derivatives of ρ and Φ. As expected, it can be easily checked that Evans' equations can be recovered by means of the above Eqs. (9)–(12).

3. ZERO-SEPARATION THEOREMS

We introduce now the functions $y_n(1,\ldots,n;\rho)$ obtained as analytic continuations over the whole space of the particle distribution functions

$g_n(1,..., n; \rho)$ by following the same prescription as for an equilibrium ensemble of hard objects[30,38–41]: $y_n(1,..., n; \rho)$ is similar to the n-particle distribution function $g_n(1,..., n; \rho)$ except that the geometric constraint due to the hard-core interactions between the n particles (no overlap between particles) is released. As a consequence,

$$g_n(1,..., n; \rho) = \prod_{i=1}^{n} \prod_{\substack{j=1 \\ j>i}}^{n} (1 + f_{ij})\, y_n(1,..., n; \rho) \tag{16}$$

According to the above definition, the y_n can be obtained in a unique way either in the framework of a grand-ensemble theory or by following the treatment of the preceding section and discarding at each step the geometric constraint between the "particles" under consideration. This latter procedure leads then to the following hierarchy of equations:

$$\begin{aligned} &\frac{1}{n\rho^{n-1}} \frac{\partial}{\partial \rho} \rho^n y_n(1,..., n; \rho) \\ &\quad = \frac{1}{nS_1(\rho)} \sum_{i=1}^{n} \left\{ \sum_{s=0}^{\infty} \frac{\rho^s}{s!} \int \cdots \int d(n+1) \cdots d(n+s)\, f_{i(n+1)} \cdots f_{i(n+s)} \right. \\ &\qquad \left. \times \prod_{\substack{j=1 \\ j \neq i}}^{n+s} \prod_{\substack{k=n+1 \\ k>j}}^{n+s} (1 + f_{jk})\, y_{n+s-1}(1,..., i-1, i+1,..., n+s; \rho) \right\} \end{aligned} \tag{17}$$

$$\begin{aligned} S_1(\rho) = 1 + \sum_{s=1}^{\infty} \frac{\rho^s}{s!} \int \cdots \int d2 \cdots d(s+1)\, f_{12} \cdots f_{1(s+1)} \\ \times \prod_{j=2}^{s+1} \prod_{\substack{k=2 \\ k>j}}^{s+1} (1 + f_{jk})\, y_s(2,..., s+1; \rho) \end{aligned} \tag{18}$$

Equations (17) and (18) can be considered as defining the y_n and it is easy to check by comparing Eqs. (11) and (12) with Eqs. (17) and (18) that Eq. (16) is indeed satisfied. The preceding equations represent the *KS-like hierarchy for the functions* y_n, which differs from its equilibrium counterpart in the "closure relation," that is, in the left-hand side of Eq. (17).

For equilibrium systems, the y_n have a simple geometric and probabilistic interpretation: $y_n^{\mathrm{eq}}(1,..., n; \rho)$ is the n-cavity distribution function, so that $(S_1^{\mathrm{eq}})^n\, y_n^{\mathrm{eq}}(1,..., n; \rho)\, d\mathbf{r}_1 \cdots d\mathbf{r}_n$ is the probability that the center of one cavity (of diameter 2σ, free of any center of particle) is in $d\mathbf{r}_1$ around $\mathbf{r}_1$,..., and the center of one cavity is in $d\mathbf{r}_n$ around $\mathbf{r}_n$. *Such an interpretation is not valid for RSA configurations.* Using probabilistic arguments, one can indeed define, in addition to the particle distribution

functions, the cavity distribution functions and some mixed cavity/particle distribution functions. However, these functions do not coincide, even outside the "core" defined by $g_n = 0$. For RSA systems, the y_n are thus analytic continuations of the particle distribution functions, but they are not equal to the cavity distribution functions.

The preceding KS-like hierarchy is a convenient starting point for deriving various "*zero-separation theorems.*"[30,38] Consider for instance Eq. (17) applied to $y_2(12;\rho)$ with the condition that $\mathbf{r}_1 = \mathbf{r}_2$. All terms of the right-hand side associated with $s > 1$ contain products like $f_{1j}(1 + f_{1j})$, $j = 3,..., s+2$, which are identically zero for hard objects of spherical symmetry. Equation (17) reduces then to

$$\frac{1}{2\rho}\frac{\partial}{\partial\rho}\rho^2 y_2(11;\rho) = \frac{1}{S_1(\rho)} \tag{19}$$

which can be formally solved to give

$$y_2(11;\rho) = \frac{2}{\rho^2}\int_0^\rho d\rho' \frac{\rho'}{S_1(\rho')} \tag{20}$$

Equation (19) or, equivalently Eq. (20), represents the *first zero-separation theorem.* It provides a new way to calculate $S_1(\rho)$, the fraction of the total surface or volume which is accessible to the center of a new particle, which *requires only knowledge of* y_2.

The treatment can be applied to higher-order functions. We obtain then

$$\frac{1}{n\rho^{n-1}}\frac{\partial}{\partial\rho}\rho^n y_n(1, 1,..., 1;\rho) = \frac{y_{n-1}(1, 1,..., 1;\rho)}{S_1(\rho)} \tag{21}$$

which can be solved to give

$$y_n(1, 1,..., 1;\rho) = \frac{n!}{\rho^n}\int_0^\rho d\rho_1 \frac{1}{S_1(\rho_1)}\int_0^{\rho_1} d\rho_2 \frac{1}{S_1(\rho_2)}\cdots \times \int_0^{\rho_{n-2}} d\rho_{n-1}\frac{\rho_{n-1}}{S_1(\rho_{n-1})} \tag{22}$$

The simplicity of the zero-separation theorems for equilibrium cavity distribution functions is lost. For instance, the relation between $y_3(111;\rho)$ and $y_2(11;\rho)$ takes the form

$$y_3(111;\rho) = \frac{3}{4}\left\{y_2(11;\rho)^2 + \int_0^1 d\alpha\,\alpha^2 y_2(11;\alpha\rho)^2\right\} \tag{23}$$

instead of $y_3^{eq}(111;\rho) = y_2^{eq}(11;\rho)^2$ obtained in the equilibrium case.[30,38,39] The complexity of Eq. (23) casts some doubts on all possible superposition approximations for $y_3(123)$.

As in equilibrium statistical mechanics,[39–41] the preceding zero-separation formulas may prove interesting either to check and improve approximate treatments of the various distribution functions or, once an approximate $y_2(12)$ is obtained, to calculate $S_1(\rho)$.

4. DIAGRAMMATIC EXPANSIONS

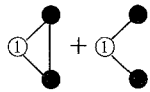
Having derived an exact hierarchy of equations for describing RSA configurations, we now face the problem of looking for solutions. Exact solutions are of course out of reach: we will see that even in one dimension, only a partial, though exact, solution was found. For RSA on lattices, different kinds of approximate truncations of exact hierarchical equations have been proposed,[11,19] but they are not easily transposable to the continuum case studied here. The approach we suggest rests on the observation that an RSA process can be roughly divided into *two regimes:* the slow asymptotic approach to the jamming limit, corresponding to "high" densities, and an initial regime, corresponding to "low to intermediate" densities. Rather than looking for a single method of approximation which tries to account for the features of both regimes, a more tractable and perhaps more powerful procedure is to study the two regimes separately. Using the fact that RSA systems do not undergo phase transitions, the results derived independently for the two regimes can then be combined to provide a description of the whole time/density range. Such a procedure was applied with some success to the two-dimensional situation where accurate interpolation formulas were given for the density dependence of $\Phi(\rho) \equiv S_1(\rho)$.[14,37]

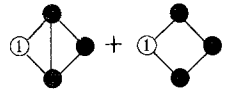
In the asymptotic regime, the available surface consists of small disconnected areas, usually refered to as targets, which can accommodate the center of one additional particle only (this property can indeed be viewed as defining the asymptotic regime). Properties of the regime are derived by the distribution of targets as a function of time. Analytical results have already been obtained by Pomeau, Swendsen, and others,[22,26–28] and we do not repeat the arguments here. We focus instead on the other regime, loosely characterized as "initial" and corresponding to low to intermediate densities (relative to the saturation density at the jamming limit).

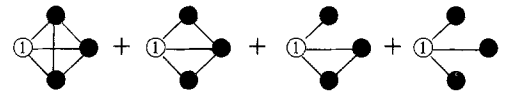
One way to generate approximate solutions is to consider expansions in powers of the density. Although it is very unlikely that they converge for high densities, such expansions may prove useful for several reasons. It has been shown, for instance, that considering the first terms of the density

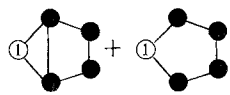
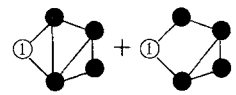
expansion of $\Phi(\rho)$ gives a good description of low- to moderate-density cases.[29] Moreover, Stell showed for equilibrium fluids that exact and approximate integral equations for the pair distribution function can be directly obtained from the density, i.e., diagrammatic, expansions.[39] Approximate integral equations, such as the Percus–Yevick equation, have proved to be powerful techniques in equilibrium statistical mechanics, and one can hope the same will be true for the RSA situation.

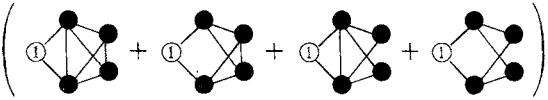
We start from the KS-like hierarchy for the functions y_n [the n-particle distribution functions are obtained by applying Eq. (16)]. From the structure of Eqs. (17) and (18), it can be seen that in order to obtain the kth term of the density expansion of y_n it is sufficient to know y_{n-1} up to the kth term and all the other distribution functions up to the $(k-1)$th term. The coefficients of the density expansions can thus be systematically determined, one after another. The starting point is provided by the property $y_1 = 1$, which is a consequence of the macroscopic uniformity of RSA systems of particles. The first terms can then be derived in a straightforward manner and we give them below as an illustration:

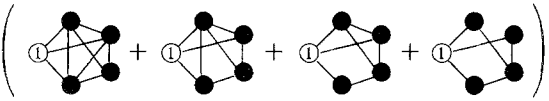
$$S_1(\rho) = 1 + \rho\{$$  $$\} + \rho^2 \left\{ \right.$$  $$\left. \right\}$$

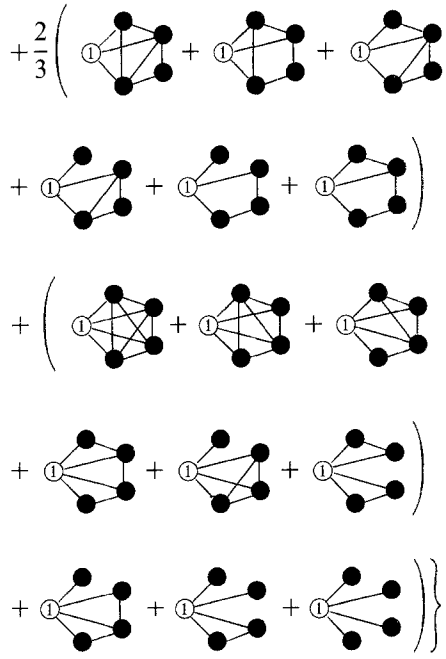
$$+ \rho^3 \left\{ \frac{2}{3} \left(\right. \right.$$  $$\left. \right)$$

$$+ \left(\right.$$  $$\left. \right) \left. \right\}$$

$$+ \rho^4 \left\{ \frac{1}{3} \left(\right.$$  $$\left. \right) + \frac{5}{6} \left(\right.$$  $$\left. \right)$$

$$+ \frac{2}{4} \left(\right.$$  $$\left. \right)$$

$$+ \frac{3}{4} \left(\right.$$  $$\left. \right)$$



(24)

$$y_2(12;\rho) = 1 + \rho\left\{\frac{2}{3}\,\textcircled{1}\!\!-\!\!\bullet\!\!-\!\!\textcircled{2}\right\} + \rho^2\left\{\frac{1}{3}\left(\;\textcircled{1}\!\!\textcircled{2}\;+\;\textcircled{1}\!\!\textcircled{2}\;\right)\right.$$

$$\left. + \frac{2}{4}\left(\;\textcircled{1}\!\!\textcircled{2}\;+\;\textcircled{1}\!\!\textcircled{2}\;+\;\textcircled{1}\!\!\textcircled{2}\;\right)\right\} + O(\rho^3) \qquad (25)$$

$$y_3(123;\rho) = 1 + \rho\left\{\frac{3}{4}\,\textcircled{1}\!\!-\!\!\bullet\!\!\begin{matrix}\textcircled{2}\\ \textcircled{3}\end{matrix} + \frac{2}{3}\left(\textcircled{1}\!\!-\!\!\bullet\!\!-\!\!\textcircled{2} + \textcircled{2}\!\!-\!\!\bullet\!\!-\!\!\textcircled{3} + \right.\right.$$

$$\left.\left. \textcircled{3}\!\!-\!\!\bullet\!\!-\!\!\textcircled{1}\right)\right\} + O(\rho^2) \qquad (26)$$

etc. The diagrammatic representation is the usual one,[42] where all bonds are f-bonds. As first noted by Widom,[13] the first three terms, up to ρ^2, of the expansion of $S_1(\rho)$ are identical to those of the expansion of the equilibrium counterpart $S_1^{eq}(\rho)$. For higher-order terms, the RSA and equilibrium expansions are different.[13,15,29]

Before giving a more general picture of density expansions for RSA configurations, we first recall the results obtained for the equilibrium situation.[39,43,44] Using Salpeter's terminology,[44]

$$S_1^{\mathrm{eq}}(\rho) = 1 + \sum_{k=1}^{\infty} \rho^k \beta_1'^{(k)\mathrm{eq}} \tag{27}$$

$$y_n^{\mathrm{eq}}(1,\ldots,n;\rho) = 1 + \sum_{k=1}^{\infty} \rho^k \beta_n'^{(k)\mathrm{eq}}(1,\ldots,n), \qquad n \geqslant 2 \tag{28}$$

where $\beta_1'^{(k)\mathrm{eq}}$ is the sum of all "*general 1-irreducible*" *diagrams* with k field points and $\beta_n'^{(k)\mathrm{eq}}(1,\ldots,n)$, $n \geqslant 2$, is the sum of all "*general* $1\cdots n$*-irreducible*" *diagrams* with k field points. A general 1-irreducible diagram is defined by the condition that each of the k field points is either "multiply connected" to point 1 or else is directly connected only to point 1 and to no other point. A general $1\cdots n$-irreducible diagram is such that each of the k field points lies on at least one continuous path between at least one pair of points selected from $1,\ldots,n$. Notice that according to the latter definition a general $1\cdots n$-irreducible diagram, $n \geqslant 2$, is also a general $1\cdots n, n+1\cdots n+p$-irreducible diagram, $p \geqslant 1$. Equations (27) and (28) can be further modified by using the "exponentiation theorem"[42] and by introducing $\beta_1^{(k)\mathrm{eq}}$ and $\beta_n^{(k)\mathrm{eq}}(1\cdots n)$ as sums of all "simple 1-irreducible" diagrams and of all "simple $1\cdots n$-irreducible" diagrams, respectively. Definitions can be found in Salpeter's paper.[44] We find that

$$S_1^{\mathrm{eq}}(\rho) = \exp\left\{\sum_{k=1}^{\infty} \rho^k \beta_1^{(k)\mathrm{eq}}\right\} \tag{29}$$

$$y_2^{\mathrm{eq}}(12;\rho) = \exp\left\{\sum_{k=1}^{\infty} \rho^k \beta_2^{(k)\mathrm{eq}}(12)\right\} \tag{30}$$

$$y_n^{\mathrm{eq}}(1\cdots n;\rho) = y_n^{\mathrm{eq,SA}}(1\cdots n;\rho) \exp\left\{\sum_{k=1}^{\infty} \rho^k \beta_n^{(k)\mathrm{eq}}(1\cdots n)\right\}, \quad n \geqslant 3 \tag{31}$$

where $y_n^{\mathrm{eq,SA}}(1\cdots n;\rho)$ is built from all the y_m^{eq}, $2 \leqslant m \leqslant n-1$, through a generalized superposition formula[39,44]:

$$y_n^{\mathrm{eq,SA}}(1\cdots n;\rho) = \prod_{m=2}^{n-1} \left[\prod_{\{m\}_n} y_m^{\mathrm{eq}}(\{m\}_n;\rho)\right]^{(-1)^{n+m+1}} \tag{32}$$

In the preceding formula, $\{m\}_n$ denotes any ordered set of m points selected from $\{1,\ldots,n\}$. In one dimension, all simple $1\cdots n$-irreducible diagrams, for $n \geqslant 3$, vanish exactly when $r_1,\ldots,r_n$ belong to the region defined by

$$\prod_{i=1}^{n} \prod_{\substack{j=1 \\ j>i}}^{n} (1+f_{ij})$$

because of geometric constraints. The Kirkwood superposition is then exact for the *particle* distribution functions (but not for the cavity distribution functions).[39,40] In higher dimensions, superposition schemes are only approximate.

The formal simplicity of diagrammatic expansions in equilibrium statistical mechanics derives from the Gibbs distribution. This simplicity is lost when going to RSA configurations. However, it can still be proven that the density expansions

$$S_1(\rho) = 1 + \sum_{k=1}^{\infty} \rho^k \beta_1'^{(k)} \tag{33}$$

$$y_n(1,\ldots,n;\rho) = 1 + \sum_{k=1}^{\infty} \rho^k \beta_n'^{(k)}(1,\ldots,n), \qquad n \geqslant 2 \tag{34}$$

correspond to diagrammatic expansions where $\beta_1'^{(k)}$ *is a linear combination of general* 1*-irreducible diagrams with* k *field points and* $\beta_n'^{(k)}(1,\ldots,n)$ *is a linear combination of general* $1\cdots n$*-irreducible diagrams with* k *field points. The coefficients of the linear combinations are rational numbers.* The result is not at all obvious, since *a priori* the coefficients of the density expansions (33) and (34) may involve *reducible* diagrams. Proof is rather lengthy and is left for Appendix A. See also ref. 15. Complexity of the RSA situation, compared to the equilibrium one, manifests itself in the fact that the coefficients with which the unlabeled general irreducible diagrams appear in $\beta_1'^{(k)}$ or $\beta_n'^{(k)}(1,\ldots,n)$ are no longer equal to 1 nor even identical to each other: compare, for instance, with Eqs. (24)–(26). The various coefficients satisfy the relations given in Appendix B, but do not lend themselves to simple recurrence formulas. The $\beta_n'^{(k)}$ can be expressed formally as

$$\begin{aligned}\binom{n+k}{n} \beta_n'^{(k)}(1,\ldots,n) &= \frac{1}{n} \sum_{i=1}^{n} \left\{ \sum_{s=0}^{\infty} \frac{1}{s!} \left[\int \cdots \int d(n+1)\cdots d(n+s)\, f_{i(n+1)} \cdots f_{i(n+s)} \right.\right. \\ &\quad \left.\left. \times \prod_{\substack{j=1 \\ j\neq i}}^{n+s} \prod_{\substack{e=n+1 \\ e>k}}^{n+s} (1+f_{je})\, \beta_{n+s-1}'^{(k-s)}(1,\ldots,i-1,i+1,\ldots,n+s) \right]_{\substack{k\text{-gen} \\ 1\cdots n \text{ irr}}} \right\}\end{aligned} \tag{35}$$

where $[\cdots]_{k\text{-gen},\, 1\cdots n\,\text{irr}}$ indicates that within the brackets all diagrams other than general $1\cdots n$-irreducible diagrams with k field points must be discarded. A formula similar to Eq. (35) holds for $\beta_1'^{(k)}$.

Another manifestation of the complexity of the RSA situation is that the "exponentiation theorem" cannot be applied. We show in Appendix C, by giving counterexamples, that there is no RSA counterpart of Eqs. (29)–(32). *As a consequence, the superposition approximation is no longer exact in one dimension:* $g_3(123;\rho)$ and $g_3^{SA}(123;\rho)$ are identical up to the ρ term, but differ for higher-order terms. The difference may be small for low and intermediate densities, but probably not for high densities close to the jamming limit. As we have already mentioned, the physical reason is that the system is sensitive to the order in which particles are introduced: as it is sometimes stated, the system has an "infinite memory." Contrary to the one-dimensional hard-rod system at equilibrium, for which all the distribution functions are known exactly, only the pair distribution function is known for the one-dimensional RSA system. Moreover, the pair distribution function is only known for $\sigma \leqslant |\mathbf{r}_1 - \mathbf{r}_2| \leqslant 2\sigma$. This is enough to determine $S_1(\rho)$ and, through Eq. (1), $\rho(t)$, but it does not provide a full characterization of the one-dimensional RSA configurations.

5. AN APPROXIMATE EQUATION FOR $g_2(12;\rho)$

Density expansions, such as those described in the preceding section, have obvious shortcomings. They probably do not converge for high densities and moreover they are not a convenient way to obtain a correct description of the pair distribution function $g_2(12;\rho)$, a quantity of primary interest to characterize RSA configurations. A fruitful alternative, widely used in equilibrium statistical mechanics, is to derive integral equations for $g_2(12)$. Stell[39] showed that the exact Ornstein–Zernike equation can be derived from the diagrammatic expansion; see also ref. 45. Use of different closure relations, which corresponds in fact to neglecting different classes of diagrams, provides different approximate equations, the most successful for hard isotropic objects being the Percus–Yevick (PY) equation.

At this stage, we mention that we have not been able to derive from the diagrammatic expansion, Eqs. (33)–(35), an *exact* equation for $g_2(12)$, which would be the RSA counterpart of the Ornstein–Zernike equation. We believe this is due to the intrinsic complexity of the RSA statistics. In what follows, we thus consider the direct derivation of *approximate* integral equations from Eqs. (33)–(35). Since we focus on approximate integral equations, more precisely on a PY-like equation, we do not expect the description to be valid in the high-density regime, close to the jamming limit: for such a regime, different methods must be employed, which predict, for instance, a logarithmic divergence at contact, in any dimension.[22,28]

The starting point is to rewrite the diagrammatic expansion in terms of different classes of diagrams:

$$y(12;\rho) = 1 + S(12;\rho) + B(12;\rho) + P(12;\rho) \tag{36}$$

$$B_2'^{(k)}(12) = S^{(k)}(12) + B^{(k)}(12) + P^{(k)}(12), \qquad k \geqslant 2 \tag{37}$$

where $S^{(k)}(12)$, $B^{(k)}(12)$, and $P^{(k)}(12)$ are linear combinations of *1, 2-series* diagrams, *1, 2-bridge* diagrams and *1, 2-parallel* diagrams, respectively, all diagrams having k field points. Definitions for these classes of diagrams are found, e.g., in ref. 42. A PY-like approximation consists of neglecting all bridge and parallel diagrams in Eqs. (36) and (37)[39]:

$$B(12;\rho) + P(12;\rho) \simeq 0 \tag{38}$$

hoping, as in the equilibrium case, that a cancellation of errors makes this approximation reasonable, at least for low to intermediate densities.[5] Consider then the coefficient $S^{(k)}(12)$: according to Eqs. (35) and (37), it can be expressed as

$$\begin{aligned}\left(\frac{2+k}{2}\right) S^{(k)}(12) &= \sum_{s=1}^{k} \frac{1}{s!} \Bigg[\int \cdots \int d3 \cdots d(s+2)\, f_{13}(1+f_{23}) \cdots f_{1(s+2)} \\ &\quad \times (1+f_{2(s+2)}) \prod_{j=3}^{s+2} \prod_{\substack{e=3 \\ e>k}}^{s+2} (1+f_{je})\, \beta_s'^{(k-s)}(23\cdots s+2) \Bigg]_{\substack{k\text{-}1,2 \\ \text{series}}}, \qquad k \geqslant 1\end{aligned} \tag{39}$$

which also corresponds formally to

$$\begin{aligned}\frac{1}{2\rho} \frac{\partial}{\partial \rho} \rho^2 S(12;\rho) &= \sum_{s=1}^{\infty} \frac{\rho^s}{s!} \Bigg[\int \cdots \int d3 \cdots d(s+2)\, f_{13}\,(1+f_{23}) \cdots f_{1(s+2)}(1+f_{2(s+2)}) \\ &\quad \times \prod_{j=3}^{s+2} \prod_{\substack{e=3 \\ e>j}}^{s+2} (1+f_{je})\, y_{s+1}(23\cdots s+2;\rho) \Bigg]_{\substack{1,2 \\ \text{series}}}\end{aligned} \tag{40}$$

[5] A more rigorous condition than Eq. (38) is to require that $(1+f_{12})[B(12)+P(12)]=0$, so that $g_2(12)=(1+f_{12})[1+S(12)]$. There is no real need for $B(12)+P(12)$ to be zero within the core in order to derive a PY equation: cf. ref. 39.

where only series diagrams are retained in the terms within the brackets. Note, however, that Eqs. (39) and (40) are *exact*, whereas in the PY equation, the series diagrams are obtained through an *approximate* formula. In the equilibrium case, Eq. (38) is a closure relation for the Ornstein–Zernike equation and is thus sufficient to derive the PY equation. *In the RSA case, for which no Ornstein–Zernike-like equation is available, we need an additional condition which specifies the procedure for obtaining an approximate* $S^{(PY)}$ *(12) directly from Eqs. (39), (40).* It is easy to show that in the equilibrium case $S^{(PY)}(12)$ is obtained from the KS hierarchy, and thus from an equation similar to Eq. (40), by replacing the exact distribution functions g_{s+1}, $s \geqslant 2$, by a generalized Kirkwood superposition approximation:

$$g_{s+1}(2, 3,..., s+2; \rho) \simeq \prod_{j=2}^{s+2} \prod_{\substack{e=2 \\ e>j}}^{s+2} g_2(je; \rho) \tag{41}$$

The preceding condition is a consequence of the structure of the series diagrams retained in the PY approximation: they are such that between two nodal points or between one nodal point and one of the root points 1 or 2, there may be only an f-bond alone or an f-bond plus a series diagram[39,45] (we recall that a nodal point is a field point through which all paths between the root points 1 and 2 pass). Simple topological considerations, when applied to the equilibrium counterparts of Eqs. (39) and (40), then lead to the condition expressed by Eq. (41).

We now retain Eq. (41) as the additional condition to derive an approximate equation for the RSA case.[6] Introducing Eq. (41) into Eq. (39) provides

$$\begin{aligned}\left(\frac{2+k}{2}\right) S^{(k)}(12) &= \sum_{s=1}^{k} \frac{1}{s!} \sum_{(\alpha\beta)} \sum_{k_{\alpha\beta}=0}^{k-s} \Bigg[\int \cdots \int d3 \cdots d(s+2)\, f_{13}(1+f_{23})\, \beta_2'^{(k_{23})}(23) \cdots \\ &\quad \times f_{1(s+2)}(1+f_{2(s+2)})\, \beta_2'^{(k_{2(s+2)})}(2, s+2) \prod_{j=3}^{s+2} \prod_{\substack{e=3 \\ e>j}}^{s+2} (1+f_{je})\, \beta_2'^{(k_{je})}(je) \Bigg]_{\substack{k\text{-}1,2 \\ \text{series}}}\end{aligned} \tag{42}$$

where $(\alpha\beta)$ denote all ordered pairs built from 2, 3,..., $s+2$, and the sum over $k_{\alpha\beta}$ is restricted by the condition that $\sum_{(\alpha\beta)} k_{\alpha\beta} = k - s$. Consider the

[6] Note that Eq. (41) is by itself a closure relation for the KS-like hierarchy and allows, in principle, the determination of $g_2(12; \rho)$ and $S_1(\rho)$. However, the resulting equation for $g_2(12; \rho)$ is very complicated and we do not pursue this direction.

general s-term of the preceding formula. It is clear that, in all series diagrams with k field points appearing within the brackets, one of the s field points 3,..., $s+2$ is a nodal point: the k_{je} field points appearing in $\beta_2'^{(k_{je})}(je)$, with j, $e=3,...,s+2$ and $e>j$, cannot be nodal points since both j and e are directly connected to 1 by an f-bond; moreover, if one of the k_{2j} field points appearing in $\beta_2'^{(k_{2j})}(2j)$, $j=3,...,s+2$, is a nodal point, then j is also a nodal point. Since the field points are dummy variables, we denote by 3 the field point selected from 3,..., $s+2$, which is a nodal point. Taking into account that none of the remaining $(s-1)$ field points 4,..., $s+2$ are connected to 2 by any path other than those passing through 3, and that when $k_{23}=0$ the point 3 must be connected to 2 by an f-bond, we rewrite Eq. (42) as

$$\begin{aligned}\left(\frac{2+k}{2}\right) S^{(k)}(12) &= \sum_{s=1}^{k} \frac{s}{s!} \sum_{k_{23}=0}^{k-s} \int d3\, f_{13}[(1+f_{23})\, \beta_2'^{(k_{23})}(23) - \delta_{0k_{23}}] \\ &\times \sum_{(\alpha\beta)\neq(23)} \sum_{k_{\alpha\beta}=0}^{k-s} \left[\int \cdots \int d4 \cdots d(s+2)\, f_{14} \cdots f_{1(s+2)} \right. \\ &\left. \times \prod_{j=3}^{s+2} \prod_{\substack{e=4 \\ e>j}}^{s+2} (1+f_{je})\, \beta_2'^{(k_{je})}(je) \right]_{\substack{k-(k_{23}+1)\text{ gen} \\ 1,2\text{-irr}}} \end{aligned} \tag{43}$$

where δ_{0k} is the Kronecker symbol and the sum over $k_{\alpha\beta}$ is restricted by the condition that $\sum_{(\alpha\beta)} k_{\alpha\beta} = k-s-k_{23}$. By permuting the order in which the sums over s and k_{23} are performed, and using Eqs. (35) and (41), we transform Eq. (43) into

$$\begin{aligned}\left(\frac{2+k}{2}\right) S^{(k)}(12) &= \sum_{k_{23}=0}^{k-1} \int d3\, f_{13}[(1+f_{23})\, \beta_2'^{(k_{23})}(23) - \delta_{0k_{23}}] \\ &\times \frac{2+k-(k_{23}+1)}{2}\, \beta_2'^{(k-k_{23}+1)}(13) \end{aligned} \tag{44}$$

Under the conditions (38) and (41), we thus derive a PY-like equation for the RSA pair distribution function, which is expressed as

$$y_2(12;\rho) = 1 + S(12;\rho) \tag{45}$$

$$S(12;\rho)+\frac{\rho}{2}\frac{\partial}{\partial\rho}S(12;\rho)$$
$$=\rho\int d3\, f_{13}\left[y_2(13;\rho)+\frac{\rho}{2}\frac{\partial}{\partial\rho}y_2(13;\rho)\right][(1+f_{23})\,y_2(23;\rho)-1] \tag{46}$$

The difference between Eq. (46) and the equilibrium PY equation is contained in the two additional terms involving derivatives with respect to ρ. Because of these latter derivatives, Eqs. (45) and (46) are not easily solvable. Indeed, by Fourier transforming Eq. (46), introducing the total pair correlation function $h(12)=g_2(12)-1$, and formally solving the differential equation in ρ, we transform Eqs. (45) and (46) into the following equation:

$$1+\rho\hat{h}(k;\rho)=\int_0^1 d\alpha\,\exp\left\{\rho\left[\hat{c}(k;\rho)-\alpha\hat{c}(k;\alpha\rho)+\int_0^1 d\alpha'\,\hat{c}(k;\alpha'\rho)\right]\right\} \tag{47}$$

where $\hat{c}(k;\rho)$ is the Fourier transform of the PY-like "direct correlation function" defined as

$$c(r;\rho)=f(r)[1+S(r)] \tag{48}$$

In deriving Eqs. (47) and (48), we used the fact that all pair functions depend only on the relative distance $r=|\mathbf{r}_1-\mathbf{r}_2|$. The left-hand side of Eq. (47) is the RSA "static structure factor": the right-hand side appears to be much more complex than its counterpart in the equilibrium PY equation, which is simply equal to $[1-\rho\hat{c}(k;\rho)]^{-1}$. Obtaining exact analytical solutions of Eqs. (47) and (48) seems then very doubtful and numerical solutions are required.

Apart from the difficulty involved in solving the PY-like equation, two major differences with the equilibrium situation should be stressed. The first one is that, when applied to a one-dimensional hard-rod system, the PY-like equation is not an exact equation: the reason is that, as discussed in Section 4, Eq. (41) is not exactly satisfied. The second difference is that knowing the pair distribution function (and for the purpose here, it does not matter whether it is known exactly or approximately) is not sufficient to determine the macroscopic properties of the system, like, for instance, $S_1(\rho)$. Additional assumptions [such as a general Kirkwood superposition scheme, an approximation of $y_2(12)$ within the "core," or an approximate interpolation formula] are required. Nonetheless, the pair distribution function is by itself a fundamental property characterizing RSA configura-

tions. To our knowledge, there is no experimental measure of RSA-like pair distribution functions yet available. This situation could change thanks, for instance, to neutron studies of ion implantation processes in semiconductors[9] or optical microscopy of configurations formed by adsorbed latexes on solid surfaces. RSA pair distribution functions of hard disks and hard spheres have been obtained at a few densities by computer simulations.[9,22] Their main feature, compared to the corresponding equilibrium pair distribution functions, is that they show almost no "structure": oscillations of the functions are strongly damped at all densities and the value of 1 is reached for interparticle separations (center-to-center) around 2.5 particle diameters. We have started studying the numerical solutions of the PY-like equation to check if they reproduce the above feature.

6. A POSSIBLE CONNECTION TO GLASSY STATES

It was emphasized by Widom that RSA produces "biased" configurations which cannot be used to describe systems at equilibrium. This "bias" can also be viewed as a major advantage: *the RSA process is a systematic, and relatively simple, way to produce nonequilibrium configurations.* As we discussed in the Introduction, it may apply to a variety of physical, chemical, biological, and ecological situations. It is tempting to increase the list by adding other nonequilibrium systems, such as glassy states obtained through a kinetic transition.[46,47] Can indeed the RSA process be used to generate glassy configurations? We will conclude the paper by discussing this question.

A first obstacle is that RSA configurations are "frozen" by definition of the model. To check that the configurations are glassy requires the introduction of some dynamics in the system of adsorbed particles. Moreover, as we argued elsewhere,[47] the simple RSA described in this paper is not appropriate since, for a continuous description of space considered here, the maximum density for RSA configurations, namely the saturation density at the jamming limit, is always *less* than the freezing density of the corresponding equilibrium system. One could think though of a slightly different procedure: instead of being initiated from an empty surface (or volume, etc.), an RSA process could start from an *equilibrium* configuration of particles on the surface (or in the volume, etc.) characterized by a *finite density* ρ_0. Such an RSA process, satisfying the conditions (i)–(iii) described in the Introduction, now has the following interesting feature: it reaches asymptotically a new jamming limit, characterized by a saturation density $\rho_s(\rho_0)$ which is *higher* than $\rho_s(\rho_0 = 0)$. By choosing appropriately the initial density ρ_0, one can both avoid crystallization of the system and generate nonequilibrium configurations having a higher density than the

freezing density. Note that the densities attainable are less than that of the random close-packed structures. In three dimensions, for instance, these latter structures are known to provide a reasonable first-order representation of simple metallic glasses[48] and they presumably correspond, too, to the metastable amorphous phase obtained with hard spheres.[49] The configurations generated by the modified RSA procedure would then be relevant for studying nonequilibrium glassy states of hard spheres produced by a kinetic transition occurring at densities lower than the random close packing.[49]

The RSA process defined above can still be described exactly with KS-like hierarchies (for the distribution functions), Eqs. (11) and (12) and Eqs. (17) and (18), associated with Eqs. (1) and (10a) for the time evolution of the density: the initial conditions ρ_0 and $\{y_n^{eq}(1,..., n; \rho_0)\}$ are of course different from the usual ones, and the one-to-one mapping between time and density must be defined on a different interval of densities $[\rho_0 \leqslant \rho < \rho_s(\rho_0)]$. It is easy to show that density expansions can be performed around ρ_0, in which all coefficients are obtained (sequentially) in terms of the equilibrium cavity distribution functions $\{y_n^{eq}(1,..., n; \rho_0)\}$, and that the approach to the jamming limit can be analytically treated as in the simple RSA case. Application of this new version of the RSA process may prove interesting in the case of a two-dimensional system of hard disks, for which the existence of glassy states is still an open question. It would then allow a systematic investigation of nonequilibrium configurations at densities lower than that of the random loose- and close-packed structures studied recently.[50]

APPENDIX A. DIAGRAMMATIC NATURE OF THE $\beta_n'^{(k)}(1,..., n)$

In this Appendix, we prove that all $\beta_n'^{(k)}(1,..., n)$, $k \geqslant 1$ and $n \geqslant 2$, satisfy the following property, which we call *property A*: $\beta_n'^{(k)}(1,..., n)$, $k \geqslant 1$ *and* $n \geqslant 2$, *is a linear combination of "general* $1 \cdots n$*-irreducible" diagrams with k field points; the coefficients of the linear combination are rational numbers.*

We show also that all $\beta_1'^{(k)}$ satisfy a similar property, which we call *property B*: $\beta_1'^{(k)}$, $k \geqslant 1$, *is a linear combination of "general 1-irreducible" diagrams with k field points; the coefficients of the linear combination are rational numbers.*

The starting point is that the coefficients $\beta_n'^{(k)}(1,..., n)$, $n \geqslant 1$, of the density expansions (33) and (34) can be systematically obtained, one after another. Indeed, introducing Eqs. (33) and (34) into Eqs. (17) and (18) and using the property $y_1 = 1$ provides

$$\binom{2+k}{2}\beta_2'^{(k)}(12)+\sum_{q=0}^{k-1}\binom{2+q}{2}\beta_2'^{(q)}(12)\,\beta_1'^{(k-q)}$$
$$=\sum_{s=1}^{k}\frac{1}{s!}\int\cdots\int d3\cdots d(s+2)\,f_{13}\cdots f_{1(s+2)}$$
$$\times\prod_{j=2}^{s+2}\prod_{\substack{e=3\\e>j}}^{s+2}(1+f_{je})\,\beta_{s+1}'^{(k-s)}(23\cdots s+2),\qquad k\geqslant 1 \tag{A1a}$$

$$\binom{n+k}{n}\beta_n'^{(k)}(1,\ldots,n)+\sum_{q=0}^{k-1}\binom{n+q}{n}\beta_n'^{(q)}(1,\ldots,n)\,\beta_1'^{(k-q)}$$
$$=\frac{1}{n}\sum_{i=1}^{n}\Bigg\{\beta_{n-1}'^{(k)}(1,\ldots,i-1,i+1,\ldots,n)$$
$$+\sum_{s=1}^{k}\frac{1}{s!}\int\cdots\int d(n+1)\cdots d(n+s)\,f_{i(n+1)}\cdots f_{i(n+s)}$$
$$\times\prod_{\substack{j=1\\j\neq i}}^{n+s}\prod_{\substack{e=(n+1)\\e>j}}^{n+s}(1+f_{je})\,\beta_{n+s-1}'^{(k-s)}(1,\ldots,i-1,i+1,\ldots,n+s)\Bigg\},$$
$$k\geqslant 1,\quad n\geqslant 3 \tag{A1b}$$

$$\beta_1'^{(1)}=\int d2\,f_{12} \tag{A2a}$$

$$\beta_1'^{(k)}=\sum_{s=2}^{k}\frac{1}{s!}\int\cdots\int d2\cdots d(s+1)\,f_{12}\cdots f_{1(s+1)}$$
$$\times\prod_{j=2}^{s+1}\prod_{\substack{e=2\\e>j}}^{s+1}(1+f_{je})\,\beta_s'^{(k-s)}(2\cdots s+1),\qquad k\geqslant 2 \tag{A2b}$$

where by convention we take

$$\beta_n'^{(0)}(1,\ldots,n)=1,\qquad n\geqslant 1 \tag{A3}$$

From Eqs. (A1a), (A2a), and (A3), one can determine directly $\beta_2'^{(1)}(12)$ and then, by using Eq. (A1b), all $\beta_n'^{(1)}(1,\ldots,n)$ one after another. On the other hand, $\beta_1'^{(2)}$ is obtained by inserting Eq. (A3) in Eq. (A2b). Knowing these coefficients, one can use Eq. (A1a) to determine $\beta_2'^{(2)}(12)$ and then sequentially all $\beta_n'^{(2)}(1,\ldots,n)$ by applying Eq. (A1b). $\beta_1'^{(3)}$ is obtainable, too, through the use of Eq. (A2b). The procedure can be repeated: once all $\beta_p'^{(q)}$, $1\leqslant q\leqslant k-1$, and all $\beta_p'^{(k)}$, $1\leqslant p\leqslant n-1$, are known, $\beta_n'^{(k)}$ is obtained by applying Eq. (A1a) if n is equal to 2 or Eq. (A1b) if n is larger than 2;

$\beta_1'^{(k+1)}$ is also determined through Eq. (A2b). Since all the coefficients can be obtained sequentially, following the above procedure, we will prove property A by *mathematical induction*. The proof then requires that:

(i) $\beta_2'^{(1)}(12)$ satisfies property A.

(ii) If all $\beta_p'^{(q)}$, $1 \leqslant q \leqslant k-1$ and $p \geqslant 2$, and all $\beta_p'^{(k)}$, $2 \leqslant p \leqslant n-1$, satisfy property A, then $\beta_n'^{(k)}$ satisfies property A, too, whatever $k \geqslant 1$ and $n \geqslant 2$.

According to Eq. (25), condition (i) is satisfied, so we focus now on condition (ii). We assume that all $\beta_p'^{(q)}$, $1 \leqslant q \leqslant k-1$ and $p \geqslant 2$, and all $\beta_p'^{(k)}$, $2 \leqslant p \leqslant n-1$, satisfy property A. $\beta_n'^{(k)}(1,..., n)$, $k \geqslant 1$ and $n \geqslant 2$, can be determined from Eqs. (A1). We consider then the right-hand side of Eqs. (A1), and, in particular, the $i=1$ contribution. All other contributions can be treated in a similar way (for $n=2$, the $i=1$ and $i=2$ contributions are actually identical). The $i=1$ contribution is itself the sum of various s contributions, $s=0, 1,..., k$. The $s=0$ contribution is zero for $n=2$ and is equal to $\beta_{n-1}'^{(k)}(2,..., n)$ for $n \geqslant 3$. By assumption, $\beta_{n-1}'^{(k)}(2,..., n)$ is a linear combination of general $2 \cdots n$-irreducible diagrams with k field points. As we noted, a general $2 \cdots n$-irreducible diagram with k field points is also a general $12 \cdots n$-irreducible diagram with k field points, so that the $s=0$ contribution is either null ($n=2$) or a linear combination of general $1 \cdots n$-irreducible diagrams with k field points ($n \geqslant 3$); the coefficients of the linear combination are rational numbers, by assumption. Consider next the $s=1$ contribution,

$$\int d(n+1)\, f_{1(n+1)} \prod_{j=2}^{n} (1+f_{j(n+1)})\, \beta_n'^{(k-1)}(2 \cdots n+1) \tag{A4}$$

By assumption, $\beta_n'^{(k-1)}(2 \cdots n+1)$ is linear combination of general $2 \cdots n+1$-irreducible diagrams with $(k-1)$ field points. Hence, whatever the diagram is, the $(k-1)$ field points lie on at least one continuous path joining the point $(n+1)$ to at least one of the points selected from 2,..., n or joining at least two of the points selected from 2,..., n. The point $(n+1)$ can then be connected to one of the $(n-1)$ root points 2,..., n either by a path appearing in one of the diagrams forming $\beta_n'^{(k-1)}$, or directly by an f-bond obtained by developing the product

$$\prod_{j=2}^{n} (1+f_{j(n+1)})$$

It may also not be connected at all to any of the points 2,..., n. The $s=1$ contribution can thus be expressed as sum of two contributions:

one contribution collecting all terms for which the point $(n+1)$ is connected, directly by an f-bond or indirectly by a continuous path involving other field points, to at least one of the $(n-1)$ root points 2,..., n, and one contribution collecting all terms for which the point $(n+1)$ is not connected to any of the $(n-1)$ root points 2,..., n. By construction, all terms of the first contribution are such that the point $(n+1)$ lies on at least one continuous path joining 1 to one of the points selected from 2,..., n; the remaining $(k-1)$ field points lie on at least one continuous path joining one pair of points selected from 2,..., n or one of the points 2,..., n to $(n+1)$, and therefore to 1 since $(n+1)$ is connected directly to 1 by an f-bond. From these topological arguments we thus derive that this first contribution is a linear combination of *general* $1 \cdots n$*-irreducible diagrams with* k *field points*. The coefficients are obviously rational numbers. On the other hand, all terms of the second contribution are such that the point $(n+1)$ is not connected to any of the points 2,..., n. The corresponding diagrams are thus *reducible*. This second contribution is obtained from all diagrams appearing in $\beta_n'^{(k-1)}(2,..., n, n+1)$ which do not involve the point $(n+1)$. As shown in Appendix B [compare with Eq. (B3b)], the part of $\beta_n'^{(k-1)}(2,..., n, n+1)$ which satisfies the latter condition is *exactly* equal to $\beta_{n-1}'^{(k-1)}(2,..., n)$. The second contribution is thus equal to

$$\left[\int d(n+1)\, f_{1(n+1)}\right] \beta_n'^{(k-1)}(2,..., n) \tag{A5}$$

Collecting these results and using Eq. (A2a), we find that the $s=1$ contribution can be written as

$$\left[\int d(n+1)\, f_{1(n+1)} \prod_{j=2}^{n} (1+f_{j(n+1)})\, \beta_n'^{(k-1)}(2,..., n+1)\right]_{\substack{k\text{-gen.} \\ 1..n\text{-irr.}}} + \beta_1'^{(1)} \beta_n'^{(k-1)}(2,..., n) \tag{A6}$$

where the symbol $[\cdots]_{k\text{-gen., 1. }n\text{-irr}}$ indicates that we retain all general $1 \cdots n$-irreducible diagrams with k field points (and only those ones) built from the term within the brackets.

We consider now the general s contribution, $s \in \{1,..., k\}$. It is equal to

$$\frac{1}{s!} \int \cdots \int d(n+1) \cdots d(n+s)\, f_{1(n+1)} \cdots f_{1(n+s)} \times \prod_{j=2}^{n+s} \prod_{\substack{e=n+1 \\ e>j}}^{n+s} (1+f_{je})\, \beta_{n+s-1}'^{(k-s)}(2,..., n+s) \tag{A7}$$

By assumption, $\beta'^{(k-s)}_{n+s-1}(2,..., n+s)$ is linear combination of general $2\cdots n+s$-irreducible diagrams with $(k-s)$ field points, except for $k=s$, where it simply reduces to 1. Generalizing the preceding treatment for $s=1$, we consider a decomposition of the s contribution according to the number t of field points selected from $(n+1),..., (n+s)$ which are connected, directly by an f-bond or indirectly by a continuous path involving other field points, to one of the root points taken from 2,..., n. The number t then runs from 0 to s. Consider first the $t=s$ contribution. All terms included in this contribution are such that the s field points $(n+1),..., (n+s)$ lie on at least one continuous path joining 1 to one of the roots points 2,..., n. The $(k-s)$ remaining field points lie on at least one continuous path joining any pair of points selected from 2,..., n or any point selected from $(n+1),..., (n+s)$ to any point selected from 2,..., n. Since the points $(n+1),..., (n+s)$ are all directly connected to 1 by an f-bond, it follows that all terms included in the $t=s$ contribution are *general* $1\cdots n$-*irreducible diagrams with k field points*. From the structure of expression (A7) and the property of the $\beta'^{(k-s)}_{n+s-1}$, it is clear that the $t=s$ contribution is a linear combination of general $1\cdots n$-irreducible diagrams, the coefficents of which are rational numbers. We consider next an arbitrary t contribution, $0\leqslant t\leqslant s-1$. It contains *reducible* diagrams and may be obtained as follows. Since the points $(n+1),..., (n+s)$ correspond to dummy variables, the t contribution can be written as C^t_s times the contribution obtained by labeling the t points $(n+1),..., (n+t)$, where C^t_s is a binomial coefficient. By definition, then, all terms forming the contribution are such that the remaining $(s-t)$ points, $(n+t+1),..., (n+s)$, are not connected, neither directly nor indirectly, to any of the root points 2,..., n. Obviously, there is no path connecting any point selected from 2,..., n, $(n+1),..., (n+t)$ to any point selected from $(n+t+1),..., (n+s)$. The "labeled" t contribution is thus obtained from the part of $\beta'^{(k-s)}_{n+s-1}(2\cdots n+s)$ containing all disconnected diagrams obtainable as a product of a diagram involving the points 2,..., n, $(n+1),..., (n+t)$ and a diagram involving $(n+t+1),..., (n+s)$. As discussed in Appendix B [compare with Eq. (B6b)], this part of $\beta'^{(k-s)}_{n+s-1}(2,..., n+s)$ is *exactly* equal to

$$\sum_{K=0}^{k-s} \beta'^{(K)}_{s-t}(n+t+1,..., n+s)\,\beta'^{(k-s-K)}_{n+t-1}(2,..., n, n+1,..., n+t) \quad \text{if } s-t\geqslant 2$$

and to

$$\beta'^{(k-s)}_{n+t-1}(2,..., n+t) \qquad \text{if } t=s-1$$

The t contribution is thus *obtained from*

$$\frac{C_s^t}{s!}\sum_{K=0}^{k-s}\left[\int\cdots\int d(n+t+1)\cdots d(n+s)\,f_{1(n+t+1)}\cdots f_{1(n+s)}\right.$$
$$\left.\times\prod_{j=(n+t+1)}^{n+s}\prod_{\substack{e=(n+t+1)\\e>j}}^{n+s}(1+f_{je})\,\beta'^{(K)}_{s-t}(n+t+1,\ldots,n+s)\right]$$
$$\left[\int\cdots\int d(n+1)\cdots d(n+t)\,f_{1(n+1)}\cdots f_{1(n+t)}\right.$$
$$\left.\times\prod_{j=2}^{n+t}\prod_{\substack{e=(n+1)\\e>j}}^{n+t}(1+f_{je})\,\beta'^{(k-s-K)}_{n+t+1}(2,\ldots,n+t)\right] \tag{A8}$$

where only the $K=0$ term must be kept when $t=s-1$. We emphasize, though, that the t term is obtained from Eq. (A8), but is not equal to it. Indeed the second factor involving the points $2,\ldots,(n+t)$ could still contain reducible diagrams, for which some of the t points $(n+1),\ldots,(n+t)$ are not connected, directly or indirectly, to at least one of the root points $2,\ldots,n$. We must keep in this second factor only those terms for which the t points $(n+1),\ldots,(n+t)$ are connected to at least one of the points $2,\ldots,n$. As proven above, it means keeping all general $1\cdots n$-irreducible diagrams with $(k-s-K+t)$ field points. The t contribution is then *equal to*

$$\sum_{K=0}^{k-s}\frac{1}{(s-t)!}\left[\int\cdots\int d(n+t+1)\cdots d(n+s)\,f_{1(n+t+1)}\cdots f_{1(n+s)}\right.$$
$$\left.\times\prod_{j=n+t+1}^{n+s}\prod_{\substack{e=n+t+1\\e>j}}^{n+s}(1+f_{je})\,\beta'^{(K)}_{s-t}(n+t+1,\ldots,n+s)\right]$$
$$\times\frac{1}{t!}\left[\int\cdots\int d(n+1)\cdots d(n+t)\,f_{1(n+1)}\cdots f_{1(n+t)}\right.$$
$$\left.\times\prod_{j=2}^{n+t}\prod_{\substack{e=(n+1)\\e>j}}^{n+t}(1+f_{je})\,\beta'^{(k-s-K)}_{n+t+1}(2,\ldots,n+t)\right]_{\substack{(k-s-K+t)\text{-gen}\\1\cdots n\text{-irr}}} \tag{A9}$$

where only the $K=0$ term must be kept when $t=s-1$.

By collecting all the preceding results, we can express the $i=1$ contribution to the right-hand side of Eqs. (A1) as

$$\sum_{s=0}^{k}\frac{1}{s!}\left[\int\cdots\int d(n+1)\cdots d(n+s)\,f_{1(n+1)}\cdots f_{1(n+s)}\right.$$
$$\left.\times\prod_{j=2}^{n+s}\prod_{\substack{e=n+1\\e>j}}^{n+s}(1+f_{je})\,\beta'^{(k-s)}_{n+s-1}(2,\ldots,n+s)\right]_{\substack{k\text{-gen}\\1\cdots n\text{-irr}}}$$

$$
+\sum_{s=1}^{k}\left[\int d(n+s)\, f_{1(n+s)}\right]\frac{1}{(s-1)!}
$$

$$
\times\left[\int\cdots\int d(n+1)\cdots d(n+s-1)\, f_{1(n+1)}\cdots f_{1(n+s-1)}\right.
$$

$$
\left.\times\prod_{j=2}^{n+s-1}\prod_{\substack{e=n+1\\ e>j}}^{n+s-1}(1+f_{je})\,\beta'^{(k-s)}_{n+s-2}(2,\ldots,n+s-1)\right]_{\substack{(k-1)\text{-gen}\\ 1\cdots n\text{-irr}}}
$$

$$
+\sum_{s=1}^{k}\sum_{t=0}^{s-2}\sum_{K=0}^{k-s}\frac{1}{(s-t)!}\left[\int\cdots\int d(n+t+1)\cdots d(n+s)\, f_{1(n+t+1)}\cdots f_{1(n+s)}\right.
$$

$$
\left.+\prod_{j=n+t+1}^{n+s}\prod_{\substack{e=n+t+1\\ e>j}}^{n+s}(1+f_{je})\,\beta'^{(K)}_{s-t}(n+t+1,\ldots,n+s)\right]
$$

$$
\times\frac{1}{t!}\left[\int\cdots\int d(n+1)\cdots d(n+t)\, f_{1(n+1)}\cdots f_{1(n+t)}\right.
$$

$$
\left.\times\prod_{j=2}^{n+t}\prod_{\substack{e=n+1\\ e>j}}^{n+t}(1+f_{je})\,\beta'^{(k-s-K)}_{n+t-1}(2,\ldots,n+t)\right]_{\substack{(k-s-K+t)\text{-gen}\\ 1\cdots n\text{-irr}}} \tag{A10}
$$

The third term of the preceding expression can be rewritten by first changing the variable K into $q=k-s-K+t$, then permuting the order in which the sums are performed according to

$$
\sum_{s=1}^{k}\sum_{t=0}^{s-2}\sum_{q=t}^{k-s+t}\leftrightarrow\sum_{q=0}^{k-2}\sum_{t=0}^{q}\sum_{s=t+2}^{t+k-q}
$$

and finally changing the variable s into $w=s-t$. By inspection of Eqs. (A1) and (A10) we first obtain that if $\beta'^{(k)}_n$ satisfies property A, it is necessarily given by Eq. (35). Using then Eq. (35) for all $\beta'^{(q)}_n$, $q\leqslant k-1$, which by assumption satisfy property A, together with Eqs. (A2a) and (A2b), we finally derive that the right-hand side of Eqs. (A1) can be exactly written as

$$
\sum_{i=1}^{n}\sum_{s=0}^{k}\frac{1}{s!}\left[\int\cdots\int d(n+1)\cdots d(n+s)\, f_{i(n+1)}\cdots f_{i(n+s)}\right.
$$

$$
\left.\times\prod_{\substack{j=1\\ j\neq i}}^{n+s}\prod_{\substack{e=n+1\\ e>j}}^{n+s}(1+f_{je})\,\beta'^{(k-s)}_{n+s-1}(1,\ldots,i-1,i+1,\ldots,n+s)\right]_{\substack{k\text{-gen}\\ 1\cdots n\text{-irr}}}
$$

$$
+\sum_{q=0}^{k-1}\binom{n+q}{n}\beta'^{(q)}_n(1,\ldots,n)\,\beta'^{(k-q)}_1 \tag{A11}
$$

so that $\beta_n'^{(k)}(1,\ldots,n)$ is indeed given by Eq. (35). This completes the proof of condition (ii).

Having proven that all $\beta_n'^{(k)}$, $k \geqslant 1$ and $n \geqslant 2$, satisfy property A, it is now a trivial matter to prove that all $\beta_1'^{(k)}$, $k \geqslant 1$, satisfy property B. According to Eq. (A2a), it is obviously true for $\beta_1'^{(1)}$. For higher-order $\beta_1'^{(k)}$, $k \geqslant 2$, given by Eq. (A2b), we can use simple topological arguments which would apply similarly to the equilibrium situation. Consider any s contribution, $2 \leqslant s \leqslant k$. Any term included in this contribution is such that all $(k-s)$ field points appearing in $\beta_s'^{(k-s)}(2,\ldots,s+1)$ lie on at least one continuous path joining one pair of points selected from $2,\ldots,s+1$ (property A). Since all field points $2,\ldots,(s+1)$ are directly connected to 1 by an f-bond, the remaining $(k-s)$ field points are "multiply connected" to point 1. The k field points are thus either directly connected only to point 1 and to no other point [which is the case for some of the points $2,\ldots,(s+1)$], or "multiply connected" to 1 [which is the case for the remaining points taken from $2,\ldots,(s+1)$ and the other $(k-s)$ field points]. This corresponds to the definition of general 1-irreducible diagrams with k field points. From the structure of the right-hand side of Eq. (A2b) and the fact that all $\beta_s'^{(k-s)}$ satisfy property A, it is moreover clear that $\beta_1'^{(k)}$ is a linear combination of general 1-irreducible diagrams, the coefficients of which are rational numbers.

APPENDIX B. ADDITIONAL PROPERTIES OF THE $\beta_n'^{(k)}(1\cdots n)$

We start from Eq. (34), where the $\beta_n'^{(k)}(1,\ldots,n)$ are linear combinations of general $1\cdots n$-irreducible diagrams with k field points. As we have noted, any general $i_1\cdots i_m$-irreducible diagram with k field points where $\{i_1\cdots i_m\}$ is any ordered set of points selected from $1,\ldots,n$ is also a general $1\cdots n$-irreducible diagram with k field points. $\beta_n'^{(k)}(1,\ldots,n)$ can thus be written as

$$\beta_n'^{(k)}(1,\ldots,n) = \sum_{m=2}^{n} \sum_{\{m\}_n} \delta_{nm}'^{(k)}(\{m\}_n) \tag{B1}$$

where the symbol $\{m\}_n$ denotes any of the (ordered) sets of m points $\{i_1\cdots i_m\}$ selected from the n points $1,\ldots,n$. The $\delta_{nm}'^{(k)}(\{m\}_n)$ is the part of $\beta_n'^{(k)}(1,\ldots,n)$ that contains only those general $1\cdots n$-irreducible diagrams with k field points which are also general $\{m\}_n$-irreducible diagrams with k field points and which moreover are such that all points taken from $\{m\}_n$ are connected to at least one field point by an f-bond (as a consequence all points selected from $\{m\}_n$ are connected to at least one other point selected

from $\{m\}_n$ by a continuous path). A first property is then that $\delta'^{(k)}_{nm}(\{m\})$, $n \geqslant m$, is independent of n:

$$\delta'^{(k)}_{nm}(\{m\}) = \delta'^{(k)}_{mm}(\{m\}) = \delta'^{(k)}_{m}(\{m\}), \qquad n \geqslant m \tag{B2}$$

Proof is obtained by noticing that whenever the $(n-m)$ particles corresponding to the set of positions built from $\{1 \cdots n\}$ by subtracting the points taken from $\{m\}_n$ become infinitely separated from each other and from the remaining m particles, the n-particle distribution function reduces exactly to the m-particle distribution function associated with the positions $\{m\}_n$; accordingly,

$$y_n(1,..., n; \rho) \to y_m(\{m\}_n; \rho) \tag{B3a}$$

$$\beta'^{(k)}_n(1,..., n) \to \beta'^{(k)}_m(\{m\}_n) \tag{B3b}$$

This is due to the fact that "interactions" between particles are short-ranged: it is valid for the RSA as well as for the equilibrium situation. Going from Eqs. (B3) to Eq. (B2) only requires the definition of $\delta'^{(k)}_{nm}$ and the short-range nature of the f-bonds.

The $\beta'^{(k)}_n(1,..., n)$ can be further decomposed by defining a "connected" and a "disconnected" part of $\delta'^{(k)}_n(\{n\})$, such that

$$\delta'^{(k)}_n(\{n\}) = \delta'^{(k)\mathrm{con}}_n(\{n\}) + \delta'^{(k)\mathrm{dis}}_n(\{n\}) \tag{B4}$$

The "connected" part $\delta'^{(k)\mathrm{con}}_n(\{n\})$ is the linear combination of those diagrams appearing in $\delta'^{(k)}_n(\{n\})$ which are such that any pair of points selected from $\{n\}$ is connected by at least one continuous path. This path passes through at least one of the k field points. The "disconnected" part is zero for $k \leqslant 1$ and $n \leqslant 3$ and otherwise can be expressed in terms of "connected" parts through

$$\delta'^{(k)\mathrm{dis}}_n(\{n\}) = \sum_{\alpha=2}^{\min\{k,N\}} \sum_{\gamma=1}^{\alpha} \sum_{n_\gamma=2}^{n-1} \sum_{\{n_\gamma\}_n} \sum_{k_\gamma=1}^{k-1} \prod_{\gamma=1}^{\alpha} \delta'^{(k_\gamma)\mathrm{con}}_{n_\gamma}(\{n_\gamma\})_n \tag{B5}$$

where the sums over n_γ, $\{n_\gamma\}_n$, and k_γ are restricted by the conditions

$$\sum_\gamma n_\gamma = n \tag{B6a}$$

$$\bigoplus_\gamma \{n_\gamma\}_n = \{n\} \tag{B6b}$$

$$\sum_\gamma k_\gamma = k \tag{B6c}$$

The symbol $\bigoplus_\gamma \{n_\gamma\}_n = \{n\}$ indicates that the α sets $\{n_\gamma\}$, $\gamma = 1,..., \alpha$, realize an exact partition of $\{n\}$, and N is equal to $n/2$ if n is even and to $(n-1)/2$ if n is odd. Equation (B5) may be derived by considering the following property of the distribution functions (a property which, for the same reasons as given above, is valid for the RSA as well as for the equilibrium situation): if the α sets $\{n_\gamma\}_n$, $\gamma = 1,..., \alpha$, realize an exact partition of $\{n\}$, with $2 \leqslant n_\gamma \leqslant n-1$ and $2 \leqslant \alpha \leqslant N$, and if the α ensembles of particles associated with the α sets of positions $\{n_\gamma\}_n$ go infinitely far from each other, then the n-particle distribution function reduces exactly to a product of n_γ-particle distribution functions, $\gamma = 1,..., \alpha$; accordingly,

$$y_n(\{n\}; \rho) \to \prod_{\gamma=1}^{\alpha} y_{n_\gamma}(\{n_\gamma\}_n; \rho) \tag{B7a}$$

$$\beta'^{(k)}_n(\{n\}) \to \sum_{k_\gamma=0}^{k} \prod_{\gamma=1}^{\alpha} \beta'^{(k_\gamma)}_{n_\gamma}(\{n_\gamma\}_n) \qquad \sum_\gamma k_\gamma = k \tag{B7b}$$

and as a consequence

$$\delta'^{(k)}_n(\{n\}) \to \sum_{k_\gamma=1}^{k-1} \prod_{\gamma=1}^{\alpha} \delta'^{(k_\gamma)}_{n_\gamma}(\{n_\gamma\}_n), \qquad k \geqslant 2 \qquad \sum_\gamma k_\gamma = k \tag{B8}$$

Going from Eq. (B8) to Eq. (B5) uses the fact that $\delta'^{(k)\mathrm{dis}}_n(\{n\})$ can be uniquely decomposed in terms collecting products of connected general irreducible diagrams such that the root points associated with these latter diagrams correspond to an exact partition of $\{n\}$. Taking moreover into account the short-range nature of the f-bonds, one finds that the decomposition of $\delta'^{(k)\mathrm{dis}}_n(\{n\})$ is that given by Eq. (B5).

By collecting all preceding results, we obtain finally

$$\beta'^{(k)}_n(\{n\}) = \sum_{m=2}^{n} \sum_{\{m\}_n} \sum_{\alpha=1}^{\min\{k,N\}} \sum_{\gamma=1}^{\alpha} \sum_{m_\gamma=1}^{m} \sum_{\{m_\gamma\}_m} \sum_{k_\gamma=1}^{k} \prod_{\gamma=1}^{\alpha} \delta'^{(k_\gamma)\mathrm{con}}_{m_\gamma}(\{m_\gamma\}_m) \tag{B9}$$

where the sums over m_γ, $\{m_\gamma\}_m$, and k_γ are restricted by the conditions

$$\sum_\gamma m_\gamma = m \tag{B10a}$$

$$\bigoplus_\gamma \{m_\gamma\}_m = \{m\} \tag{B10b}$$

$$\sum_\gamma k_\gamma = k \tag{B10c}$$

APPENDIX C. ON THE SUPERPOSITION APPROXIMATION

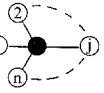
Comparing Eqs. (25) and (26) with their equilibrium counterparts, it is tempting to write y_n in the following compact form:

$$y_2(12;\rho)=\frac{2}{\rho^2}\int_0^\rho d\rho'\,\rho'\exp\left\{\sum_{k=1}^{\infty}\rho'^k\beta_2^{(k)}(12)\right\} \tag{C1}$$

$$y_n(1,\ldots,n;\rho)=y_n^{\mathrm{SA}}(1,\ldots,n;\rho)\frac{n}{\rho^n}\int_0^\rho d\rho'\,\rho'^{n-1}$$
$$\times\exp\left\{\sum_{k=1}^{\infty}\rho'^k\beta_n^{(k)}(1,\ldots,n)\right\},\qquad n\geqslant 3 \tag{C2}$$

where $\beta_n^{(k)}(1,\ldots,n)$, $n\geqslant 2$, would be a linear combination of simple $1\cdots n$-irreducible diagrams with k field points and $y_n^{\mathrm{SA}}(1,\ldots,n;\rho)$ would be defined by a formula similar to Eq. (32). Equations (C1) and (C2) would then be the RSA equivalent of Eqs. (30) and (31). It is indeed easy to check that Eq. (C2) is true up to order ρ, with

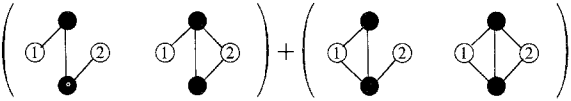
$$\beta_n^{(1)}(1,\ldots,n)=\beta_n^{(1)\mathrm{eq}}(1,\ldots,n)= \tag{C3}$$



and that Eq. (C1) is true up to order ρ^3 with

$$\beta_2^{(1)}(12)=\beta_2^{(1)\mathrm{eq}}(12)= \tag{C4a}$$

$$\beta_2^{(2)}=\frac{2}{3}\left(\right)+\left(\right) \tag{C4b}$$



$\beta_2^{(3)}(12)$ is linear combination of simple 1, 2-irreducible diagrams with three field points, but its expression is too long to be reproduced here. Unfortunately, Eqs. (C1) and (C2) are no longer valid for higher-order terms. For instance, the ρ^2 term of the expansion of $y_3(123)$ is actually given by

$$\begin{aligned}\beta_3'^{(2)}(123)=&\{\tfrac{3}{5}[\beta_3^{(2)}(123)+\tfrac{1}{2}\beta_3^{(1)}(123)^2]\\&+\tfrac{3}{4}\beta_3^{(1)}(123)[\beta_2'^{(1)}(12)+\beta_2'^{(1)}(13)+\beta_2'^{(1)}(23)]\\&+[\beta_2'^{(2)}(12)+\beta_2'^{(2)}(13)+\beta_2'^{(2)}(23)+\beta_2'^{(1)}(12)\,\beta_2'^{(1)}(13)\\&+\beta_2'^{(1)}(12)\,\beta_2'^{(1)}(23)+\beta_2'^{(1)}(13)\,\beta_2'^{(1)}(23)]\}\\&+\tfrac{1}{20}\{\beta_3^{(1)}(123)[\beta_2'^{(1)}(12)+\beta_2'^{(1)}(13)+\beta_2'^{(1)}(23)]\\&+\beta_2'^{(1)}(12)\,\beta_2'^{(1)}(13)+\beta_2'^{(1)}(12)\,\beta_2'^{(1)}(23)\\&+\beta_2'^{(1)}(13)\,\beta_2'^{(1)}(23)\}\end{aligned} \tag{C5}$$

where $\beta_3^{(2)}(123)$ is linear combination of simple 123-irreducible diagrams with two field points; all other coefficients have already been defined. The contribution within the first curly brackets of the right-hand side is that predicted by Eq. (C2). The presence of an additional contribution in the right-hand side of Eq. (C5) thus proves the inadequacy of Eq. (C2).

Two comments can be made. First, even when geometric constraints impose that the simple 123-irreducible diagrams vanish as is the case in the expansion of $g_3(1, 2, 3)$ in one dimension, the correction to Eq. (C2) persists: as seen then from Eq. (C5), *the superposition approximation is not exact in one dimension.* A similar conclusion could be reached for higher-order distribution functions. Second, the size of the correction appears quite small, at least at the order ρ^2. It probably increases as the power of ρ increases so that the superposition approximation is certainly wrong at high densities, close to the jamming limit. However, the superposition approximation may be reasonably good for low and intermediate densities. Such a statement should of course be tested numerically.

Equation (C5) has in turn consequences for the ρ^4 term of the expansion of $y_2(12; \rho)$. It is indeed straightforward to derive that

$$3\beta_2'^{(4)}(12) = \left\{ \beta_2^{(4)}(12) + \beta_2^{(3)}(12)\,\beta_2^{(1)}(12) + \tfrac{1}{2}\beta_2^{(2)}(12)[\beta_2^{(2)}(12) + \beta_2^{(1)}(12)^2] + \frac{1}{4!}\beta_2^{(1)}(12)^4 \right\} + \frac{1}{90}\left\{ \text{①—②} + \text{①—②} \right\} \tag{C6}$$

where $\beta_2^{(4)}(12)$ is a linear combination of simple 12-irreducible diagrams with four field points. The contribution within the first curly brackets is that given by the application of Eq. (C1), and the second contribution measures the correction to Eq. (C1). Here again, the size of the correction seems rather small, but it is expected to increase as the power of ρ increases.

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