Random sequential adsorption of mixtures

J. Talbot and P. Schaaf*
Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90024
(Received 3 January 1989)

We present a theory that describes the random sequential adsorption of a two-component mixture of hard disks of greatly differing diameters on a flat surface. The jamming limit of the large disks can be obtained from a numerical solution of two coupled first-order differential equations. In the special case of a mixture of disks and point particles the equations take on a simple form, and the kinetics and jamming limit can be determined essentially exactly for certain ranges of the adsorption rate constants.

I. INTRODUCTION

The random sequential adsorption (RSA) model is defined by the following rules: (i) objects are placed at random in a d-dimensional volume; (ii) if the last placed object overlaps with any of those already present it is immediately removed; and (iii) otherwise it is permanently fixed (i.e., no diffusion is allowed). The process usually begins from an empty volume and continues until the jamming limit, that is until it is impossible to place further objects.

The model has a long and interesting history.[1–5] In the early days of computer simulation it was believed that equilibrium configurations could be generated with a RSA algorithm. However, it was quickly realized that the RSA configurations are fundamentally different from their equilibrium counterparts.[3] Although inapplicable to equilibrium fluids, the RSA model in two dimensions does have important applications to the adsorption of proteins[6] and latexes[7] on solid surfaces. Like many statistical-mechanical problems, exact solutions for the jamming limit and kinetics of the RSA process exist only in one dimension.[1–4] In two dimensions most of our information comes from numerical studies. In particular, the jamming limit for disks adsorbing on a flat, uniform surface has been determined as 54.7%.[5] In any dimension d, the coverage θ, close to the jamming limit, varies with time as $\theta_\infty-\theta(t)\sim t^{-1/d}$, a result first conjectured by Feder[8] and later proved by Pomeau[9] and Swendsen.[10] At low to intermediate coverages the rate of adsorption can be expressed as a power series in the coverage. Recently we have found the exact values for the coefficients of this series up to the third order for the one-component hard-disk system.[11] Our expression is accurate up to a coverage of about 30%–35% (i.e., 55%–64% of the coverage in the jamming limit).

To our knowledge there has been only one study of the RSA of mixtures. Barker and Grimson investigated the adsorption of mixtures of lattice objects of different shapes but with the same size on a square lattice by means of computer simulation.[12] In this paper we present a theoretical analysis of a continuum case, namely, a two-component mixture of hard disks adsorbing on a flat uniform surface. The theory is applicable when the disks are very different in size. An interesting feature of this system is that it is possible to determine the jamming limit of the large disks from the numerical solution of two coupled first-order differential equations. In the one-component case, or when the two radii are similar, the nature of the adsorption process undergoes a distinct change in character as the jamming limit is approached. This can be understood in terms of the subdivision of the available area into small disconnected pieces ("target areas") at high coverage.[5] As a result of this complication there is, as yet, no theory that predicts the jamming limit coverage for the single-sized hard-disk systems. However, for a mixture of large and small particles, as long as the small ones do not adsorb too slowly compared with the large, it turns out that the large particles are prevented from ever reaching a density where the the asymptotic kinetics (for them alone) are applicable. The small particles continue to adsorb after the large disks have reached their jamming limit. It is a simple matter to determine the remaining fraction of the surface that will be covered by the small disks, since in this region they behave almost like the one-component system, for which we know from simulations that the jamming limit is 54.7% of the available surface.

Our analysis is, in general, approximate. However, in the limit case of disks and point particles the results are essentially exact as long as the point particles adsorb sufficiently rapidly.

II. THEORY

Consider a mixture of disks of radii r_A and r_B, with $r_A \ll r_B$, adsorbing on a flat uniform surface of area $\mathcal{A}$. At time $t=0$ the disks adsorb onto the empty surface at rates k_A and k_B per unit area. Let $N_A(t)$ and $N_B(t)$ denote the number of each species adsorbed at time t.

We first consider the probability $P_B(N_A,N_B)$ that a large disk arriving randomly on the surface will adsorb given that there are already N_A and N_B adsorbed particles of type A and B, respectively. For this event to occur the center of the closest adsorbed particle must be at least a distance $r_{AB}=r_A+r_B$ or $r_{BB}=2r_B$ from the center of the incoming particle, depending on whether this nearest adsorbed particle is small or large, respectively. The exclusion circles corresponding to the latter situation are illustrated in Fig. 1. In geometrical terms the

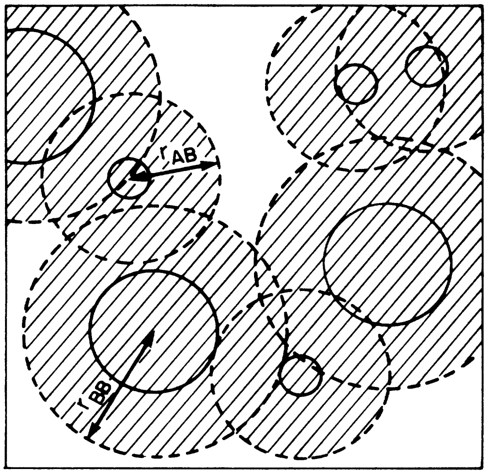

FIG. 1. Illustration of the concept of exclusion circles. For the particular configuration shown, the shaded area cannot be occupied by the center of an incoming large (B) disk. r_{AB} and r_{BB} denote the radii of the AB and BB exclusion circles, respectively.

required probability $P_B(N_A,N_B)$ is equal to the fraction of the total surface that the unshaded area in Fig. 1 represents. To calculate $P_B(N_A,N_B)$ imagine first removing all the small particles from the surface. The fraction of the area now available to a new B disk ϕ_{BB} can be expressed as a power series in the coverage $\theta_B=N_B\pi r_B^2/\mathcal{A}$,

$$\phi_{BB}(N_A,N_B)=\sum_{i=0}^{\infty}S_{i,B}\theta_B^i \ . \tag{1}$$

In general the $S_{i,B}$ are functions of N_A, r_A, and r_B (although we are imagining a situation in which the small disks have been removed, they could have influenced the placement of the B's). Equation (1) is simply a generalization of our result for the one-component system.[11] In the Appendix we demonstrate that $S_{0,B}=1$, $S_{1,B}=-4$, $S_{2,B}=6\sqrt{3}/\pi+\alpha(r_A/r_B)\theta_A+O(\theta_A^2)$, and $S_{3,B}=1.4069+O(\theta_A)$, where $\theta_A=N_A\pi r_A^2/\mathcal{A}$ represents the coverage of the large disks. We further show that $\alpha(r_A/r_B)\rightarrow 0$ as $r_A/r_B\rightarrow 0$.

Now consider the original configuration (including the small disks) once more. The adsorption probability is less than ϕ_{BB} as a result of the presence of the small particles. Precisely we have

$$P_B(N_A,N_B)=\phi_{BB}Q_{AB} \ . \tag{2}$$

Q_{AB} represents the conditional probability that, given that the center of the large incoming disk lands in the area $\mathcal{A}\phi_{BB}$, it lands in an area containing a circular region of radius r_{AB} free from small disks.

In the limit $r_A \ll r_B$, the large particles only slightly influence the correlations of the smaller ones; their effect is simply to reduce the available surface area. At time t the A disks are contained in a surface of approximate area

$$\mathcal{A}'=\mathcal{A}-\pi r_{AB}^2 N_B(t) \ . \tag{3}$$

So we can define the effective density of A disks within this area,

$$\rho_A^{\text{eff}}=N_A(t)/\mathcal{A}' \ . \tag{4}$$

The distribution of centers of small disks is nearly random as long as their effective density is not too high (for point particles $r_A=0$, the distribution is *always* random). From our previous study of the RSA of a one-component system of hard disks, it turns out that, as long as ρ_A^{eff} is smaller than 5%, the exclusion circles of the A disks do not overlap to an appreciable extent. Therefore the associated "spare surface" (i.e., the fraction of the surface available to the center of a new disk) ϕ is accurately given by $\phi=1-N_A\pi r_{AA}^2|\mathcal{A}'$, and the probability of finding a circle of radius r_{AB} free from the centers of A disks is

$$Q_{AB}=(1-\pi r_{AB}^2/\mathcal{A}')^{N_A} \ . \tag{5}$$

This equation is easily interpreted as follows: $\pi r_{AB}^2/\mathcal{A}'$ is the probability of finding *one* A disk within the circle of radius r_{AB}. One minus this quantity is then the probability that this single disk lies outside the region. Taking the N_Ath power gives the chance that *all* N_A particles lie outside the region.

By combining Eqs. (1) and (5) we find the following expression for the adsorption rate of B disks:

$$\frac{dN_B}{dt}=\mathcal{A}k_B\phi_{BB}\left[1-\frac{\pi r_{AB}^2}{\mathcal{A}(1-\pi r_{AB}^2\rho_B)}\right]^{N_A} , \tag{6}$$

or in terms of the surface densities ρ_B $(=N_B/\mathcal{A})$ and ρ_A $(=N_A/\mathcal{A})$,

$$\frac{d\rho_B}{dt}=k_B\phi_{BB}\left[1-\frac{\pi r_{AB}^2\rho A}{N_A(1-\pi r_{AB}^2\rho_B)}\right]^{N_A} . \tag{7}$$

For large systems $(N_A\rightarrow\infty)$ this may be conveniently expressed as [using the well-known result that $e^x=\lim_{n\rightarrow\infty}(1+x/n)^n$],

$$\frac{d\rho_B}{dt}=k_B\phi_{BB}\exp\left[\frac{-\pi r_{AB}^2\rho_A}{1-\pi r_{AB}^2\rho_B}\right] . \tag{8}$$

The adsorption rate for the small disks is determined as follows. For one of these disks to adsorb it must first land in an area unoccupied by large disks, which together exclude roughly a fraction $\rho_B\pi r_{AB}^2$ of the total area to the smaller disks. This approximation becomes more accurate as r_A/r_B decreases and is exact in the case of point particles. Now, assuming that it does not land on top of a B disk, the incoming small disk sees an effectively monodisperse RSA configuration of A disks at a density ρ_A^{eff} and will adsorb at the appropriate rate. Combining these two factors we obtain

$$\frac{d\rho_A}{dt}=k_A\phi(\theta_A^{\text{eff}})(1-\pi r_{AB}^2\rho_B) , \tag{9}$$

where $\theta_A^{\text{eff}}=\pi r_A^2\rho_A^{\text{eff}}$ and $\phi(\theta)$ is the one-component RSA function given in Ref. 11.

Equations (8) and (9) are coupled first-order differential equations describing the kinetics of the RSA of two kinds of disks of greatly differing diameters. They can be conveniently expressed in terms of the dimensionless variables $\theta_A=\pi r_A^2\rho_A$, $\theta_B=\pi r_B^2\rho_B$, $x_A=[(r_A+r_B)/r_A]^2$, $x_B=[(r_A+r_B)/r_B]^2$, and $\tau=\pi r_B^2 k_B t$,

$$\frac{d\theta_A}{d\tau}=\kappa(r_A/r_B)^2\phi(\theta_A^{\text{eff}})(1-x_B\theta_B)\ , \tag{10}$$

$$\frac{d\theta_B}{d\tau}=\phi_{BB}(\theta_A,\theta_B)\exp\left[\frac{-x_A\theta_A}{1-x_B\theta_B}\right]\ , \tag{11}$$

where we have introduced the relative rate constant $\kappa=k_A/k_B$. Numerical integration yields θ_A and θ_B. We expect the jamming limit of the large disks $\theta_B(\infty)$ to be highly accurate as long as the disk diameters are very different. We return to the question of accuracy in the discussion. On the other hand, Eqs. (10) and (11) cannot be expected to give an accurate value for the jamming limit of the small particles, since we only know the surface exclusion function $\phi(\theta)$, to third order in the coverage, and in any case, as we have already remarked, the nature of the adsorption process changes near the jamming limit. However, since the small disks behave effectively almost like a one-component system in the reduced area $\mathcal{A}'$ it is a simple matter to deduce the following approximate expression for the final (combined) jamming limit from a knowledge of $\theta_B(\infty)$:

$$\theta_{A+B}(\infty)=\theta_B(\infty)+(1-\pi r_{AB}^2\rho_B)\theta_\infty$$
$$=\theta_B(\infty)+(1-x_B\theta_B)\theta_\infty\ , \tag{12}$$

where θ_∞ is the one-component value determined from simulation 0.547.

There is a simple limiting form of the rate equations (8) and (9) when the small disks shrink to point particles $r_A\to 0$. The points have no effect on each other, but, once adsorbed, they exclude the centers of large disks from a circle of radius r_B. The coupled differential equations describing the adsorption become

$$\frac{d\psi_A}{d\tau}=\kappa(1-\theta_B) \tag{13}$$

and

$$\frac{d\theta_B}{d\tau}=\phi_{BB}(\theta_B)\exp\left[\frac{-\psi_A}{1-\theta_B}\right]\ , \tag{14}$$

where $\psi_A=\pi r_B^2\theta_A$. If we knew $\phi_{BB}(\theta_B)$ rigorously we could determine the *exact* kinetics for any value of κ. Fortunately if κ is not too small it suffices to know $\phi_{BB}(\theta_B)$ to second or third order. For the special case of point particles, we show in the Appendix that the expansion of ϕ_{BB} in θ_B is the same as in the one-component case up to the order of θ_B^3. Thus for points we have

$$\phi_{BB}(\theta_B)=1-4\theta_B+\frac{6\sqrt{3}}{\pi}\theta_B^2+\left[\frac{40}{\pi\sqrt{3}}-\frac{176}{\pi^2}\right]\theta_B^3+O(\theta_B^4)\ . \tag{15}$$

The geometrical factor $\alpha(r_A/r_B)$ [Eq. (A11)] is rigorously equal to zero in this case.

III. DISCUSSION

We see from Eqs. (10) and (11) that the RSA of a mixture of disks on a surface is characterized by two parameters: $\kappa=k_A/k_B$ and the ratio r_A/r_B. In the limiting case of a mixture of disks and points we are left with only the parameter κ.

From the derivation of Eqs. (10) and (11) we know that for our theory to be valid it is required that (i) $r_A/r_B\ll 1$; (ii) $\theta_B(\infty)<35\%$ so that ϕ_{BB} remains valid up to third order in the coverage; and (iii) $\theta_A^{\text{eff}}<5\%$ when $\theta_B(\tau)\to\theta_B(\infty)$. The last condition ensures that Eq. (5) accurately describes the adsorption of the smaller disks. For given values of κ and r_A/r_B we solved Eqs. (10) and (11) using the fourth-order Runge-Kutta algorithm.

There is a minimum value of κ, $\kappa_{\min}$ (a function of r_A/r_B) below which the large disks adsorb sufficiently rapidly so that their final coverage is over 35%. We have determined that when the A particles are points, $\kappa_{\min}$ is almost equal to 0.7. Figure 2 shows the jamming coverage of the large particles as a function of r_A/r_B for different values of κ ranging from 1 to 5. Note first that $\theta_B(\infty)$ is a highly insensitive function of r_A/r_B for a given κ. This implies that $\kappa_{\min}\approx 0.7$ is the lower limit of validity for our theory, for any value of r_A/r_B up to about 0.2. Moreover, Fig. 2 also illustrates that, as expected, $\theta_B(\infty)$ is a decreasing function of both r_A/r_B for a given value of κ and vice versa. For the values of κ that we considered $(0.7<\kappa<5)$, Eqs. (10) and (11) do not converge to a constant value for $\theta_B(\infty)$ when r_A/r_B is greater than about 0.3. We conclude that our theory is definitely invalid when the size ratio is greater than this value.

We can determine whether requirement (ii) is satisfied by examining the time dependence of θ_A and θ_B—see Fig. 3. From the observed values of $\theta_A(\tau)$ and $\theta_B(\tau)$ we can show that

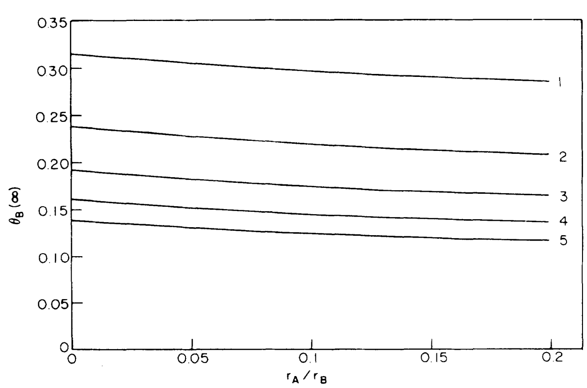

FIG. 2. Jamming limit of the large disks $\theta_B(\infty)$ as a function of the radius ratio r_A/r_B obtained by solving Eqs. (10) and (11). The numbers labeling each curve refer to the relative rate constant $\kappa=k_A/k_B$. The equations do not converge to a jamming limit for $r_A/r_B>0.3$.

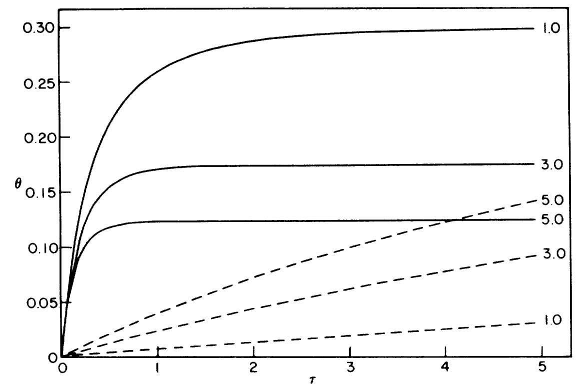

FIG. 3. Coverage θ of the large (solid line) and small (dashed line) disks as a function of the reduced time $\tau=\pi r_B^2 k_B t$, obtained by solving Eqs. (10) and (11). The results shown are for $r_A/r_B=0.1$ and the values labeling each curve refer to the relative rate constant $\kappa=k_A/k_B$.

$$\theta_A^{\text{eff}}(\tau)=\theta_A(\tau)/[1-x_B\theta_B(\tau)]$$

is indeed less than 0.05 when $\theta_B(\tau)$ has almost reached its asymptotic value.

We solved Eqs. (10) and (11) with ϕ_{BB} up to third order in θ_B [Eq. (15)]. Inclusion of the term $\alpha(r_A/r_B)\theta_A\theta_B^2$ [Eq. (A15)] has a negligible effect on $\theta_A(\tau)$ and $\theta_B(\tau)$. Indeed the two cases (with and without this term) are indistinguishable on the scale of Fig. 3. The reasons for this result are clear: When κ is small, θ_B reaches its jamming limit while θ_A is still small so that $\theta_B \gg \theta_A$. On the other hand, when κ is large, the A disks adsorb much more rapidly than the large ones so that $\theta_B(\infty)$ will be very small. Therefore in this case it is only necessary to use ϕ_{BB} to second order in the coverage, so that the terms $\theta_A\theta_B^2$ can be neglected.

Finally, in Fig. 4 we represent the variation of $\theta_B(\infty)$ as a function of κ for three different values of r_A/r_B. Once again we observe only a small variation of $\theta_B(\infty)$ with r_A/r_B. Although our theory does not hold for $\kappa<0.7$, we know the exact jamming limit for $\kappa=0$ (the one-component system). We can obtain an estimate for $\theta_B(\infty)$ for $0<\kappa<0.7$ by extrapolating the known curve to $\kappa=0$. These extrapolations are also shown in Fig. 4.

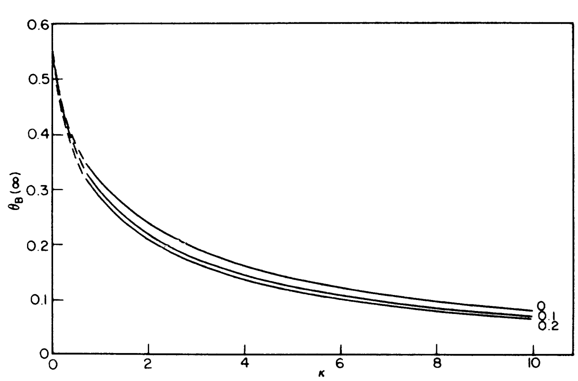

FIG. 4. Jamming limit of the large disks $\theta_B(\infty)$ as a function of the relative rate constant $\kappa=k_A/k_B$, obtained by solving Eqs. (10) and (11) [or (13) and (14) for points]. The numbers labeling each curve refer to the radius ratio r_A/r_B. The dashed curves are extrapolations of the numerical results to the known one-component value of 0.547.

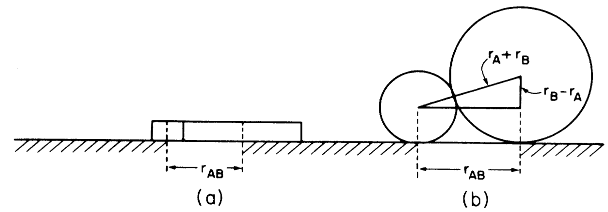

FIG. 5. Side-on view of two possible adsorption geometries: (a) the disk model $r_{AB}=r_A+r_B$; (b) the spherical model $r_{AB}=2\sqrt{r_A r_A}$.

A complete assessment of the accuracy of the theory would require comparison with computer simulation, which we do not attempt here. What we have attempted to do above is to identify the limits of κ and r_A/r_B for which the theory is *definitely* accurate.

We conclude by mentioning one more aspect of the problem. Up until now we have been considering a strictly two-dimensional model with additive disk diameters. This may be the best model for some proteins adsorbing from solution. However, in other cases (e.g., for mixtures of latex particles) it may be more appropriate to regard the adsorbing species as spherical—see Fig. 5. In this case the AB exclusion circle is given by twice the geometric mean of the sphere radii: $r_{AB}=2\sqrt{r_A r_B}$. If we let $\lambda=r_A/r_B$, Eqs. (8) and (9) become

$$\frac{d\theta_A}{d\tau}=\kappa\lambda^2\phi(\theta_A^{\text{eff}})(1-4\lambda\theta_B) \tag{16}$$

and

$$\frac{d\theta_B}{d\tau}=\phi_{BB}(\theta_B)\exp\left[\frac{-4\theta_A/\lambda}{1-4\lambda\theta_B}\right]. \tag{17}$$

Unfortunately, these equations are not as useful as Eqs. (10) and (11). The problem is that the small spheres are not effective in excluding area from the larger ones. It is instructive to consider the proportions $r_{AA}:r_{AB}:r_{BB}$. For the disk model this is $\lambda:(1+\lambda)/2:1$. The most favorable case is for $\lambda=0$, i.e., $0:\frac{1}{2}:1$ (r_{AA}, r_{AB} and r_{BB} are maximally separated). In the sphere model we find $\lambda:\sqrt{\lambda}:1$, and $\lambda=0$ is now highly unfavorable: 0:0:1. The "best" choice, $\lambda=\frac{1}{4}$ gives $\frac{1}{4}:\frac{1}{2}:1$. Although Eqs. (16) and (17) might describe the kinetics reasonably well in this case, they do not converge to a value for $\theta_B(\infty)$.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant Nos. CHE-86-04038, DMR-84-21383, and CHE-85-01019, and PRF 18122-AC6 and by the Centre National de la Recherche Scientific. We are grateful to Professor Bill Gelbart, Professor Daniel Kivelson, Professor Charles Knobler, and, in particular, Professor Howard Reiss for helpful comments.

APPENDIX

In this appendix we wish to prove the following assertions: (i) assuming that the term $S_{2,B}$ in Eq. (1) takes the form

$$S_{2,B}=\frac{6\sqrt{3}}{\pi}+\alpha(r_A/r_B)\theta_A+O(\theta_A^2)\ , \quad \text{(A1)}$$

then $\alpha(r_A/r_B)\to 0$ as $r_A/r_B\to 0$, and, (ii) that the expansion of ϕ_{BB} in a power series of θ_B is identical to the one-component function ϕ up to third order when the A particles are points $r_A=0$. For convenience, and without loss of generality we set $\mathcal{A}=1$ in what follows.

The demonstration of the above results require us to determine how the number density of pairs of large disks $N_2^{BB}(r,N_A,N_B)$, characterized by the center-center distance r, varies with N_B. A pair BB can be defined as follows: Each B disk excludes a circle of radius r_{BB} to the center of another B disk. Two B disks form a pair of separation r when their exclusion circles overlap. Let $A_{BB}(r)$ denote the area common to the two exclusion circles of the pair—see Fig. 6. To determine

$$[\partial N_2^{BB}(r,N_A,N_B)/\partial N_B]_{N_A}\ ,$$

we follow the same arguments as in Ref. 11. Consider a particular B disk which is already adsorbed. Place the origin of a polar coordinate system (r,θ) at the center of this particle. If a new disk is to adsorb in a surface element $r\,dr\,d\theta$ the following conditions must be satisfied: (i) There should be a circular region centered on $r\,dr\,d\theta$ of radius at least r_{BB} free from the centers of B disks, and, (ii) there must exist a circular region of radius r_{AB} devoid of A disks.

It can be shown that the probability p_1 for event (i) is

$$p_1=1-[\pi r_{BB}^2-A_{BB}(r)]N_B+O(N_B^2)\ . \quad \text{(A2)}$$

Let us now determine p_2, the probability of event (ii).

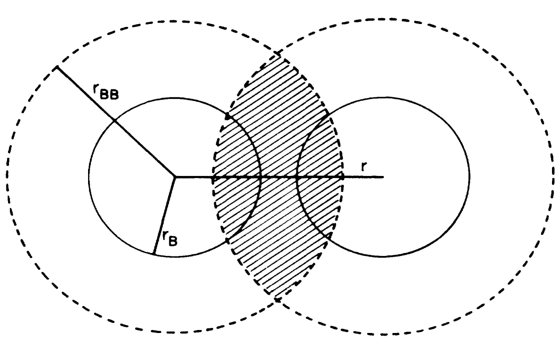

FIG. 6. Illustration of the quantity $A_{BB}(r)$—the area common to two BB exclusion circles separated by a distance r.

We know that the previously adsorbed B disk excludes a circular region of radius r_{AB} to the centers of A disks. Let $A_{AB}(r)$ denote the area common to two r_{AB} exclusion circles with their centers separated by r. It should be obvious that there cannot be a center of A disk in the overlapping region. Therefore event (ii) occurs if there is no center of an A disk in the remaining area $\pi r_{AB}^2-A_{AB}(r)$. Hence

$$p_2=1-[\pi r_{AB}^2-A_{AB}(r)]\frac{N_A}{1-\pi r_{AB}^2N_B+O(N_B^2)}+O(N_A^2)\ . \quad \text{(A3)}$$

When $r_A=0$ (point particles), $A_{AB}(r)=0$, and p_2 is then rigorously equal to

$$p_2=\left[1-\frac{\pi r_B^2}{1-\pi r_B^2N_B}\right]^{N_A}\ . \quad \text{(A4)}$$

The quantity $N_A/[1-\pi r_{AB}^2N_B+O(N_B^2)]$ represents the effective density of A disks on the surface not occupied by B disks. Let ϕ_B denote the probability that a particle of type B adsorbs *anywhere* on the surface. In the case of point particles we have

$$\phi_B=\phi_{BB}\left[1-\frac{\pi r_B^2}{1-\pi r_B^2N_B}\right]^{N_A}\ , \quad \text{(A5)}$$

whereas in the case $r_A\neq 0$ we have to lowest order in N_A and N_B

$$\phi_B=1-\pi r_{BB}^2N_B-\pi r_{AB}^2N_A+O(N_iN_j)\ , \quad \text{(A6)}$$

where $i=A,B$ and $j=A,B$.

Finally the probability that the new B disk forms a pair of separation r with a previously adsorbed B disk is

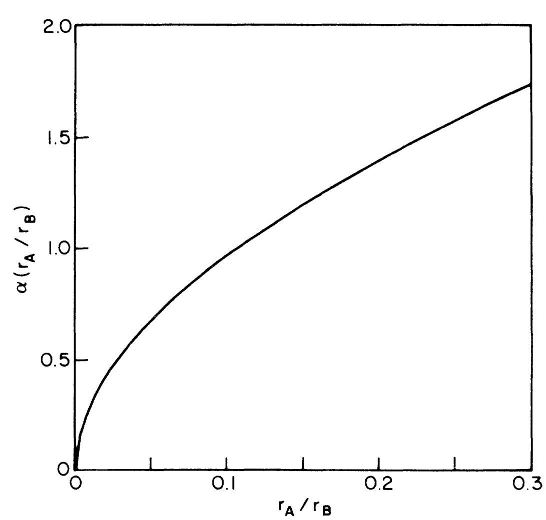

FIG. 7. Geometrical factor $\alpha(r_A/r_B)$, Eq. (A15) as a function of the radius ratio r_A/r_B. Note that $\alpha(r_A/r_B)\to 0$ as $r_A/r_B\to 0$.

$$\frac{\partial N_2^{BB}(r,N_A,N_B)}{\partial N_B}dr = N_B 2\pi r p_1 p_2 \frac{1}{\phi_B} dr \ . \tag{A7}$$

Using expression (1) for ϕ_{BB} up to order N_B, we have for point particles

$$\frac{\partial N_2^{BB}(r,N_A,N_B)}{\partial N_B} = 2\pi r[1+N_B A_{BB}(r)]N_B + O(N_B^3) \ . \tag{A8}$$

This equation is identical to the equation describing the evolution of pairs in the one-component system. It follows directly from Ref. 11 that $\phi_{BB}(N_A,N_B)$ has the same expansion in θ_B up to third order as in a one-component system.

When $r_A \neq 0$ we obtain, using Eqs. (A2), (A3), (A6), and (A7),

$$\frac{\partial N_2^{BB}(r,N_A,N_B)}{\partial N_B} = 2\pi r[1+N_B A_{BB}(r) + N_A A_{AB}(r)]N_B + O(N_i N_j) \ . \tag{A9}$$

Integration leads to

$$N_2^{BB}(r,N_A,N_B) = \pi r N_B^2[1+N_A A_{AB}(r)] + 2\pi r \frac{N_B^3}{3} A_{BB}(r) \ . \tag{A10}$$

Using Eqs. (1) and (3) in Ref. 11 we then obtain

$$\phi_{BB} = 1 - 4\theta_B + \frac{6\sqrt{3}}{\pi}\theta_B^2 + 1.4069\theta_B^3 + \alpha(r_A/r_B)\theta_B^2\theta_A \ , \tag{A11}$$

where

$$\alpha(r_A/r_B) = \frac{8}{\pi^3 r_{BB}^4 r_A^2}\int_{r_{BB}}^{r_{BB}+2r_A} 2\pi r A_{AB}(r) A_{BB}(r) dr \ . \tag{A12}$$

Simple geometric considerations show that

$$A_{AB}(r) = 2r_{AB}^2 \arccos(r/2r_{AB}) - r(r_{AB}^2 - r^2/4)^{1/2} \tag{A13}$$

and

$$A_{BB}(r) = 2r_{BB}^2 \arccos(r/2r_{BB}) - r(r_{BB}^2 - r^2/4)^{1/2} \ . \tag{A14}$$

By taking the limit $r_A/r_B \to 0$ it can be shown that

$$\alpha(r_A/r_B) \to 0 \ . \tag{A15}$$

Figure 7 shows $\alpha(r_A/r_B)$ as a function of r_A/r_B.

*Permanent address: Institut Charles Sadron Centre National de la Recherche Scientifique et Université Louis Pasteur, 6 rue Boussingault, 67083 Strasbourg CEDEX, France.

[1]A. Rényi, Publ. Math. Inst. Hung. Acad. Sci. **3**, 109 (1958) [Transl. Math. Stat. Prob. **4**, 203, (1963)].
[2]J. K. MacKenzie, J. Chem. Phys. **37**, 723 (1962).
[3]B. Widom, J. Chem. Phys. **44**, 3888 (1966).
[4]J. J. González, P. C. Hemmer, and J. S. Høye, Chem. Phys. **3**, 228 (1974).
[5]E. L. Hinrichsen, J. Feder, and T. Jøssang, J. Stat. Phys. **44**, 793 (1986).
[6]J. Feder and I. Giaever, J. Colloid Int. Sci. **78**, 144 (1980).
[7]G. Y. Onoda and E. G. Liniger, Phys. Rev. A **33**, 715 (1986).
[8]J. Feder, J. Theor. Biol. **87**, 237 (1980).
[9]Y. Pomeau, J. Phys. A **13**, L193 (1980).
[10]R. H. Swendsen, Phys. Rev. A **24**, 504 (1981).
[11]P. Schaaf and J. Talbot, Phys. Rev. Lett. **62**, 175 (1989).
[12]G. C. Barker and M. J. Grimson, Mol. Phys. **63**, 145 (1988).