Random sequential adsorption of anisotropic particles. II. Low coverage kinetics

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We study the kinetics of random sequential adsorption (RSA) of anisotropic bodies (rectangles, ellipses, spherocylinders or, more precisely, discorectangles, and needles) at low- to-intermediate coverages. In this regime, the adsorption probability can be expressed as a power series in the coverage. We calculate numerically the second- and third-order coefficients of the series and compare the results to simulation data. The results for the low-coverage kinetics are then combined with the asymptotic results of Paper I [J. Chem. Phys. 97, 5212 (1992)] to construct approximate equations for the adsorption probability over the entire coverage range. While the equations provide a reasonably good description of the RSA kinetics, they produce unsatisfactory estimates of the saturation coverages. The effect of particle shape on the adsorption kinetics and surface structure is discussed. Finally, the available surface function is compared with that corresponding to equilibrium configurations of the adsorbed particles.

I. INTRODUCTION

In the preceding companion paper,1 hereafter referred as I, we investigated the jamming limit and asymptotic behavior of the random sequential adsorption (RSA) of anisotropic particles. A more complete description of the time evolution of both the density and the structure of the adsorbed phase is the subject of the present paper. From a practical point of view, it is important to derive simple analytical equations which describe the whole process (recall for instance that, although old, the quest for equations of state in equilibrium systems remains an attractive field of research2,3).

As noted in Paper I, the adsorption kinetics for the RSA of anisotropic particles is governed by a "generalized Langmuir equation,”

$$\frac{d\theta}{dt} = k_a \int d\Omega f(\Omega) \Phi[\theta(t), \Omega],$$

where $k_a$ is the adsorption rate constant which is set to unity. $f(\Omega)$ is the probability distribution for the orientation of incoming particles, and $\Phi[\theta(t), \Omega]$ is the probability of adding a new particle with orientation $\Omega$ to the surface when the coverage is $\theta$. We restrict here ourselves to a uniform distribution, i.e., $f(\Omega) = 1/2\pi$. The purpose of the simulations and theories is then to determine $\Phi = \int_0^{2\pi} f(\Omega) \Phi[\theta(t), \Omega] d\Omega$, which we call the averaged available surface function, and hence the time dependent coverage.

Except for some one-dimensional problems,4-6 the available surface function (ASF) cannot be obtained exactly. However, a fruitful approach consists in dividing the kinetics into different regimes, to which analytical techniques can be applied. A detailed discussion of the kinetics in the high-coverage, or asymptotic, regime is given in Paper I.

The starting point of the present study is to calculate a low-coverage expansion, which represents the exact limit for short times. The method and details of the numerical calculation of the expansion coefficients are given in Sec. II. Combining these results with those of the asymptotic regime,1 we build various interpolation formulas, which are compared to simulation data in Sec. III. In many experimental systems the adsorbed molecules bind strongly to solid surfaces and do not desorb on the time scale of the experiments,7-12 whereas other systems exhibit a rapid surface diffusion.13 In the latter case, the configurations on the surface rearrange rapidly by diffusion between successive particle additions and the adsorbed particles can be considered in equilibrium on the surface (but not necessarily with the particles in the bulk). Section IV outlines a procedure to derive an equation for the averaged ASF, $\Phi_{eq}$, of systems in equilibrium; it is deduced from an equation of state for fluids composed of hard-convex bodies that was proposed by Boublik14 based on scaled particle theory. The resulting functions are compared to RSA simulation data to illustrate the differences between the kinetics of RSA and that of adsorption with surface diffusion.

II. LOW-COVERAGE EXPANSION

The low-coverage expansion of the ASF provides a systematic description of the short-time kinetics of RSA processes. In the case of spherical particles, surface exclusion effects from preadsorbed particles have a simple physical meaning, which can be described by the following geometrical arguments:15,16 starting from an empty surface, corresponding to $\Phi = 1$, the ASF is progressively decreased...
since one must subtract the exclusion areas of the adsorbed particles. At very low coverage, the exclusion areas do not overlap. As the coverage increases, the actual exclusion surface is no longer sum of the individual exclusion surfaces of the particles and overlap effects must be taken into account; corrections can be systematically applied by considering, first, pairs of particles with overlapping exclusion areas, denoted \( A_{2} \), and more generally, \( k \) tuplets of particles with common overlapping exclusion area \( A_{k}(r_{1}, r_{2}, \ldots, r_{k}) \). The ASF can then be expressed as an alternate series,

\[
\Phi = \sum_{k=0}^{\infty} (-1)^{k} \frac{\theta^{k}}{k!} \int \cdots \int g^{(k)}(r_{1}, r_{2}, \ldots, r_{k}; \theta)
\]

\[\times A_{k}(r_{1}, r_{2}, \ldots, r_{k})/(\pi \sigma^{2}/4)^{k} dr_{1} \cdots dr_{k}, \tag{2}\]

where \( \theta \) is the surface coverage, \( \sigma \) the disk diameter, and \( g^{(k)}(r_{1}, r_{2}, \ldots, r_{k}; \theta) \) the \( k \)-particle distribution function. From Eq. (2), it is easy to show that the property of uniformity is sufficient to determine exactly the two first coefficients of the expansion. Thus to order \( \theta^{2} \), the coefficients are identical for RSA and equilibrium systems. To go further, in particular for the third coefficient of the expansion, the assumption on the nature of the process (irreversible or "reversible") must be introduced in the calculation of the distribution functions.\(^{17}\) Schaaf and Talbot\(^{18}\) have calculated the third coefficient for disks and Talbot et al.\(^{19}\) for spheres in three dimensions. The fourth coefficient was obtained for disks by Dickman et al.\(^{20}\) and by Given.\(^{21}\)

To describe the kinetics of RSA for particles of arbitrary shape, Tarjus et al.\(^{16}\) have derived an exact Kirkwood-Salsburg-type hierarchy for the distribution functions. Then, using a diagrammatic algebra, each coefficient of the density expansion can be obtained as a combination of diagrams where all bonds are \( f \) bonds, where \( f \) is a Mayer function, equal to \((-1)\) when two particles overlap and 0 otherwise. As a consequence, the averaged ASF can be written to the third order as

\[
\Phi = 1 - 2 B_{2} \theta + (2 B_{2}^{2} - \frac{1}{2} B_{3}) \theta^{2} + [3 B_{2} B_{3} - \frac{1}{2} (R_{3} + R_{4}) - B_{4}'] \theta^{3}, \tag{3}\]

where \( B_{i} \) denotes the \( i \)th (equilibrium) virial coefficient and \( B_{i}' \) represents the additional coefficient appearing in the RSA process. This latter coefficient is the sum of two Mayer diagrams,

\[
\nu_{a} = \frac{1}{2} \int \cdots \int d\mathbf{r}_{1} \cdots d\mathbf{r}_{k}, \tag{4}\]

where solid and dashed lines denote \( f \) and \((1+f)\) bonds, respectively. For spherical objects, the first three virial coefficients, \( B_{1}, B_{2}, B_{3} \), as well as the specific term \( B_{4}' \) (Ref. 18) are known analytically. For convex anisotropic particles, only \( B_{2} \) has a simple analytical form,\(^{22}\)

\[
B_{2} = 1 + \frac{P^{2}}{4\pi A}, \tag{5}\]

where \( A \) is the proper area and \( P \) is the perimeter of the object. Calculation of third- and higher-order virial coefficients requires extensive use of the Monte Carlo method. Some numerical values for the third and fourth virial coefficients of ellipses, rectangles, needles, and spherocylinders (discocylinders) were calculated previously by us,\(^{23}\) using the method of Ree and Hoover.\(^{24}\) We have computed here the additional RSA term, \( B_{4}' \), and completed the previous calculations. Tables I and II list the values of \( B_{3}/B_{3}^{0} \) and \( B_{4}/B_{4}^{0} \), while the values of \( B_{4}'/B_{4}^{0} \) are displayed in Table III. Note that \( B_{3}/B_{3}^{0} \) and \( B_{4}/B_{4}^{0} \) are monotonically decreasing functions of elongation, whereas \( B_{4}'/B_{4}^{0} \) is a monotonically increasing function of elongation. As a result of this

### Table I. Reduced third virial coefficient for unaligned hard ellipses, rectangles, and spherocylinders, for various aspect ratios \( \alpha \). Results were computed with the original procedure of Ree and Hoover (100 independent runs, \( 10^{5} \) \( \alpha \) configurations per run).

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>Ellipses</th>
<th>Rectangles</th>
<th>Spherocyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.782 ± 0.001</td>
<td>0.770 ± 0.002</td>
<td>0.782 ± 0.001</td>
</tr>
<tr>
<td>2</td>
<td>0.750 ± 0.001</td>
<td>0.750 ± 0.002</td>
<td>0.756 ± 0.001</td>
</tr>
<tr>
<td>4</td>
<td>0.677 ± 0.001</td>
<td>0.696 ± 0.003</td>
<td>0.689 ± 0.001</td>
</tr>
<tr>
<td>5</td>
<td>0.651 ± 0.001</td>
<td>0.675 ± 0.003</td>
<td>0.672 ± 0.001</td>
</tr>
<tr>
<td>6</td>
<td>0.631 ± 0.001</td>
<td>0.658 ± 0.004</td>
<td>0.655 ± 0.001</td>
</tr>
<tr>
<td>15</td>
<td>0.561 ± 0.001</td>
<td>0.588 ± 0.009</td>
<td>0.582 ± 0.001</td>
</tr>
</tbody>
</table>

### Table II. Reduced fourth virial coefficient for unaligned hard ellipses, rectangles, and spherocylinders, for various aspect ratios \( \alpha \). Results were computed with the original procedure of Ree and Hoover (100 independent runs, \( 10^{5} \) \( \alpha \) configurations per run).

<table>
<thead>
<tr>
<th>( \alpha )</th>
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<th>Rectangles</th>
<th>Spherocyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.532 ± 0.002</td>
<td>0.508 ± 0.001</td>
<td>0.532 ± 0.002</td>
</tr>
<tr>
<td>2</td>
<td>0.467 ± 0.003</td>
<td>0.466 ± 0.001</td>
<td>0.477 ± 0.002</td>
</tr>
<tr>
<td>4</td>
<td>0.325 ± 0.004</td>
<td>0.360 ± 0.002</td>
<td>0.361 ± 0.002</td>
</tr>
<tr>
<td>5</td>
<td>0.272 ± 0.004</td>
<td>0.322 ± 0.002</td>
<td>0.318 ± 0.002</td>
</tr>
<tr>
<td>6</td>
<td>0.227 ± 0.005</td>
<td>0.290 ± 0.002</td>
<td>0.283 ± 0.002</td>
</tr>
<tr>
<td>15</td>
<td>0.073 ± 0.010</td>
<td>0.144 ± 0.003</td>
<td>0.136 ± 0.002</td>
</tr>
</tbody>
</table>

### Table III. Reduced RSA coefficient \( \beta_{4}'/\beta_{4}^{0} \) for unaligned hard ellipses, rectangles, and spherocylinders, for various aspect ratios \( \alpha \). Results were computed with the original procedure of Ree and Hoover (300 independent runs, \( 10^{5} \) \( \alpha \) configurations per run).

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>Ellipses</th>
<th>Rectangles</th>
<th>Spherocyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.127 ± 0.001</td>
<td>0.130 ± 0.001</td>
<td>0.127 ± 0.001</td>
</tr>
<tr>
<td>2</td>
<td>0.127 ± 0.001</td>
<td>0.130 ± 0.001</td>
<td>0.128 ± 0.002</td>
</tr>
<tr>
<td>4</td>
<td>0.137 ± 0.001</td>
<td>0.132 ± 0.001</td>
<td>0.131 ± 0.002</td>
</tr>
<tr>
<td>5</td>
<td>0.142 ± 0.002</td>
<td>0.135 ± 0.001</td>
<td>0.134 ± 0.002</td>
</tr>
<tr>
<td>6</td>
<td>0.147 ± 0.002</td>
<td>0.138 ± 0.001</td>
<td>0.139 ± 0.002</td>
</tr>
<tr>
<td>15</td>
<td>0.167 ± 0.004</td>
<td>0.157 ± 0.002</td>
<td>0.159 ± 0.003</td>
</tr>
<tr>
<td>( \infty )</td>
<td>0.193 ± 0.001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
latter feature, the RSA process differs more rapidly from the equilibrium situation when the aspect ratio is large, even at low coverages (see Figs. 1–4). Moreover, the low-coverage expansion diverges from the simulation curve at lower and lower coverages when the aspect ratio of the particle increases, which suggests that the radius of convergence of the series diminishes with increasing elongation. This may be interpreted as a preliminary signature of the intermediate needlelike regime discussed in I, a regime that cannot be reproduced by a low-coverage expansion.

Contrary to the disk case,15 but like the 3D sphere case,19 Figs. 1–3 show that for moderate and large aspect ratios, the curves obtained from the second-order expansion, $\Phi_{\bar{\rho}}$, do not intersect the x axis, so that the approximate $\Phi_{\bar{\rho}}$'s have no zeros. It is easy to check that, to order $\theta^3$, the equation $\Phi_{\bar{\rho}} = 0$ has real roots only if the reduced third virial coefficient $B_y/B_z^2 > 2/3$. Table I indicates that this is the case for ellipses if the aspect ratio is less than $\approx 4$, and for rectangles and spherocylinders if the aspect ratio is less than $\approx 5$. We note that for disks in two dimensions $B_y/B_z^2 > 2/3$, whereas $B_y/B_z^2 < 2/3$ for spheres in three dimensions. Finally, the third term of the expansions of $\Phi$ is always positive, at least when using the numerical values of Table I. We have then the following inequality: $\Phi_{\bar{\rho}}^{RSA} \geq \Phi_{\bar{\rho}}$, as is shown in Figs. 1–4.

III. APPROXIMATE THEORIES

Since we now have equations for the kinetics in the low- and high-coverage regimes, we would like to be able to combine them in some way so as to provide an accurate approximate description of the kinetics over the entire coverage range and, if possible, predict the saturation coverage for a given aspect ratio $\alpha$. 

FIG. 1. Comparison of the adsorption probability $\Phi^{RSA}$ from simulation of rectangles with the corresponding low-coverage expansion to first, second, and third order. $\Phi_{FIT1}$, and $\Phi_{FIT2}$.
It is shown in Paper I that the asymptotic power law can be expressed in the form

$$\Phi = d[\Theta_\alpha(\infty) - \Theta_\alpha]$$

(6)

where $d$ is independent of the coverage and varies slowly with the aspect ratio $\alpha$ (less than algebraic dependence). Based on the form of Eq. (3) (low-coverage expansion) and Eq. (6) (asymptotic regime), the following two functions are proposed as interpolation formulas:

$$\Phi_{FIT1}(x) = (1 - x)^{4}(1 + c_1 x + d_2 x^2),$$

(7)

$$\Phi_{FIT2}(x) = \frac{(1 - x)^4}{(1 + d_1 x + d_2 x^2)},$$

(8)

where $x = \Theta_\alpha/\Theta_\alpha(\infty)$; $c_1$, $c_2$, $d_1$, $d_2$, and $\Theta_\alpha(\infty)$ are fitting parameters which are determined by matching the Taylor series of the above two functions with the known low-coverage expansion, Eq. (3), to third order (see Tables IV–VI). Although the equations are approximate, they offer the possibility of a complete kinetic description of the process and a prediction of the saturation coverage by simply knowing the first virial-like coefficients and the asymptotic power law.

A similar approach was applied to disks in two dimensions$^{25}$ and spheres in three dimensions$^{19}$ with reasonable success. The predicted jamming limit for disks, 0.553, compares well with the value from simulation, 0.547. The corresponding values for the addition of hard spheres to a volume are 0.365 (estimate) and 0.382 (simulation). In both cases, the fitting functions were in good agreement with the simulation data; Eq. (8) was the most accurate. Dickman et al.$^{20}$ used the low-coverage series in time in conjunction with the asymptotic power law for disks to construct Padé approximants which yielded an excellent
prediction of the jamming limit (0.547 88). We have tried their method for ellipses and spherocylinders and found that it does not lead to satisfying results.

The interpolation formulas for rectangles, ellipses, and spherocylinders are compared to the simulation data in Figs. 1, 2, and 3. The simulation procedures employed here are the same as those outlined in Paper I with the exception that no acceleration procedure was used. Simulations for each aspect ratio included 500 independent runs consisting of $10^5$ trials each. Note how $\Phi_{\text{FIT2}}$ is virtually indistinguishable from the simulation data for each of the different geometries up to $\alpha \approx 5$, beyond which deviations become apparent. $\Phi_{\text{FIT1}}$ is less accurate than $\Phi_{\text{FIT2}}$, but generally improves as the particles become longer, except for rectangles, where it deviates slightly at high coverage for $\alpha = 15$.

Estimates of the saturation coverage, $\theta_\infty$, for rectangles, ellipses, and spherocylinders are listed in Tables IV, V, and VI. The simulation values listed were obtained by us in Paper I. These predictions are somewhat disappointing, although they follow a consistent trend. The saturation coverage is plotted vs the inverse of the aspect ratio $\alpha$ for ellipses, rectangles, and spherocylinders in Fig. 1 of Paper I. Neither of the fitting functions succeeds in predicting the maximum in these curves near $\alpha = 2$. The estimated coverages begin at too high values and decrease monotonically as $\alpha$ increases.

For $\alpha > 5$, the estimates are low and worsen as the particles become longer. It is easy to show that for particles of large aspect ratios the fitting functions lead to an inexact dependence on the aspect ratio $\alpha$ for the jamming limit coverage $\theta_\infty$. When $\alpha$ becomes very large, the reduced virial coefficients, $B_\alpha^{(c)} / B_\alpha^{(c)-1}$, tend to the reduced virial coefficients of the needles. This result can be easily extended.
to the successive additional terms of the RSA expansion; in particular, $B_4' / B_3'$ approaches the needle value for large $\alpha$. Starting from Eq. (3) and Eqs. (7) and (8), the determination of the saturation coverage is achieved by solving the polynomial equations,

$$
\left(3 - \frac{4}{3} \frac{B_3}{B_2} - \frac{4}{3} \frac{B_4}{B_2^2} \right) B_3^* \theta^2 + 4 \left(2 - \frac{3}{2} \frac{B_3}{B_2^2} \right) B_2^* \theta^2 + 10 B_2^* \theta^2 + 20 = 0 \quad (\text{FIT1}),
$$

$$
\left(3 + \frac{4}{3} \frac{B_3}{B_2} + \frac{4}{3} \frac{B_4}{B_2^2} \right) B_3^* \theta^2 - \left(8 + 6 \frac{B_3}{B_2^2} \right) B_2^* \theta^2 + 12 B_2^* \theta^2 - 4 = 0 \quad (\text{FIT2}).
$$

Introducing the variable $\gamma = \theta - \theta^* B_2$, one obtains that Eq. (9) has no strictly positive real roots when $\alpha$ becomes very large. Therefore, $\Phi_{\text{FIT1}}$ cannot be used for determining $\theta^*$ for very elongated particles. Equation (10) admits a strictly positive real root, $\gamma^*(\alpha)$, which converges towards a nonzero limit ($\gamma^*_1 = 2.175$) when $\alpha \to +\infty$. As the second virial coefficient, $B_2(\alpha)$, goes as $\alpha$ for large $\alpha$ [see Eq. (5)], the interpolation formulas $\Phi_{\text{FIT2}}$ thus leads to saturation coverages that behave as $1/\alpha$ when $\alpha \to +\infty$, while the correct scaling law is $\alpha^{-1(1+2v_2)}$. The discrepancy between the estimates and the simulation results can certainly be attributed to the fact that the fitting functions do not take into account the intermediate needlelike regime (see Paper I), which becomes important at high elongations. Note in Figs. 1, 2, and 3 how the low-coverage expansions diverge from the simulation curves at lower and lower coverages as the particle length increases. The radius of convergence of the power series is certainly reduced due to the increased significance of the needlelike regime. Thus using only the low- and high-coverage regimes for a numerical prediction of the jamming limit produces unsatisfactory results. However, the overall agreement of the fitting functions with the simulated $\theta(\alpha)$ is still quite good despite these difficulties. Note also how, for the short particles, the third-order expansion diverges at a significantly higher coverage.

### Table IV

<table>
<thead>
<tr>
<th>$\Phi_{\text{FIT1}}$</th>
<th>$\Phi_{\text{FIT2}}$</th>
<th>Simulations</th>
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</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>$c_1$</td>
<td>$c_2$</td>
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<tr>
<td>1</td>
<td>1.382</td>
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<tr>
<td>1.5</td>
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</tr>
<tr>
<td>2</td>
<td>1.344</td>
<td>0.920</td>
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<tr>
<td>5</td>
<td>1.129</td>
<td>0.552</td>
</tr>
<tr>
<td>15</td>
<td>0.887</td>
<td>0.256</td>
</tr>
</tbody>
</table>

### Table V

<table>
<thead>
<tr>
<th>$\Phi_{\text{FIT1}}$</th>
<th>$\Phi_{\text{FIT2}}$</th>
<th>Simulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>$c_1$</td>
<td>$c_2$</td>
</tr>
<tr>
<td>1</td>
<td>0.788</td>
<td>0.375</td>
</tr>
<tr>
<td>2</td>
<td>1.346</td>
<td>0.928</td>
</tr>
<tr>
<td>4</td>
<td>1.184</td>
<td>0.686</td>
</tr>
<tr>
<td>5</td>
<td>1.111</td>
<td>0.580</td>
</tr>
</tbody>
</table>

FIG. 4. Comparison of the adsorption probability $\Phi_{\text{RSA}}$ from simulation of needles ($\alpha \to \infty$) with the corresponding low-density expansion to first, second, and third order. No interpolation formulas are constructed for needles since they have no jamming limit.

higher coverage than the second-order expansion. For \( \alpha > 4 \), however, the third-order expansion begins to diverge at a lower coverage than the second-order expansion. The same behavior was found in the RSA of spheres to a three-dimensional space.

The inaccurate predictions for the weakly elongated particles are more puzzling since there is virtually no needlelike regime and the low-coverage expansion describes the kinetics over a wide range of coverage. One would expect an accuracy comparable to that for spherical particles. However, a close examination of the asymptotic regime may offer some insight. As discussed in Paper I, the asymptotic regime for weakly elongated ellipses and spherocylinders is made of two successive regions: one whose kinetics follow a \( t^{-1/2} \)-power law and corresponds to the filling of nonselective targets, and a second with a \( t^{-1/3} \) kinetics which corresponds to the filling of selective targets. As \( \alpha \) increases, the \( t^{-1/2} \) region shrinks and for \( \alpha \approx 1.5 \) there is no trace of \( t^{-1/2} \) behavior. Numerical results for the power-law exponents obtained from simulation confirm these arguments: The effective exponents for \( \alpha < 1.5 \) lie between \(-1/3\) and \(-1/2\). However, only the power law describing the final asymptotic regime is incorporated in the fitting functions: \( t^{-1/2} \) for \( \alpha = 1 \) (disks) and \( t^{-1/3} \) as soon as \( \alpha \) is different from 1. Therefore, the interpolation formulas do not take into account the first region of the asymptotic regime for weakly elongated objects and predict an unphysical discontinuity in \( \theta_\infty(\alpha) \) for \( \alpha = 1 \). It gives accurate results when compared with Monte Carlo

\[ \theta \approx 1.25. \] However, this is not sufficient to explain the absence of maximum at \( \alpha = 2 \) for ellipses and spherocylinders and \( \alpha = 1.6 \) for rectangles (in Paper I, we have argued that for weakly elongated rectangles the relevant elongation parameter which allows to compare rectangles and squares to ellipses and spherocylinders is not the aspect ratio \( \alpha \), but \( e = \sqrt{1 + \alpha^2}; \alpha = 1.6 \) corresponds then to \( e = 2 \)). For such elongations, there is no trace of \( t^{1/2} \) regime in the simulations. As, in addition, there is no detectable contribution of the intermediate needlelike regime, we expect that the poor quality of the predictions based on Eqs. (7) and (8) for moderate elongations is related to an unsatisfactory description of the coverage expansion by the third-order approximation.

Figure 5 displays coverage-vs-time data for disks, ellipses, and spherocylinders. Note how, up to 20 time units, the curve for disks lies above all of the others. Since we know that ellipses and spherocylinders with \( \alpha \approx 4 \) have higher saturation coverages than disks, we can infer that the curves for these aspect ratios must cross the curve for disks at some \( t > 20 \). Note also that, for \( t < 20 \), the spherocylinder curves all lie above the corresponding ellipse curves. This can be, at least partially, related to the difference between the second virial coefficients of ellipses and spherocylinders at the same aspect ratio \( \alpha; B_2(\alpha) \) is always larger for an ellipse than for a spherocylinder, and the difference increases with \( \alpha;^{23} \) as the coverage \( \theta \) goes initially as \( t \sim B_2 t^2 + \cdots \) [see Eqs. (1) and (2)], a smaller \( B_2 \) corresponds to a faster initial increase. For longer times, higher-order coefficients must be included, which leads to compensation effects and progressively reduces the difference between the ellipse and spherocylinder cases. As can be seen from Tables V and VI, the coverages attained at the jamming limit are almost identical for ellipses and spherocylinders of same aspect ratio. For illustration, we also show in Figs. 6 and 7 configurations of moderately elongated ellipses and spherocylinders (\( \alpha = 4 \)), respectively, at high coverage.

### IV. ADSORPTION WITH SURFACE EQUILIBRIUM VS RSA

The ASF for equilibrium configurations may be conveniently obtained from an equation of state, thus eliminating the need for additional simulations. Here we use the semiempirical equation for two-dimensional fluids of convex particles proposed by Boublik:

\[
Z(\theta) = \frac{P}{\rho kT} = \frac{1}{1 - \gamma} + \frac{\gamma \theta(1 + \gamma \theta/8)}{(1 - \theta)^2},
\]

where \( \gamma \) is a nonsphericity parameter given by

\[
\gamma = \frac{P^2}{4\pi A}.
\]

where \( P \) is the perimeter and \( A \) is the proper area of the particle. The equation of state (11), which is based on scaled particle theory, is believed to be one of the most accurate available. Cuesta and Frenkel\(^{26} \) have shown that it gives accurate results when compared with Monte Carlo
FIG. 5. Coverage vs time for spherocylinders and ellipses of various elongations. The corresponding curve for disks is included for comparison.

Simulations of hard ellipses, at least for aspect ratios $\alpha<6$. In general, the accuracy of theories for anisotropic fluids decreases with particle elongation. However, we hope that Eq. (11) provides a reasonable description for more elongated particles. This can only be verified by comparison with Monte Carlo simulations. The equilibrium ASF can be calculated from the so-called osmotic equation of state.

$$\ln \left( \Phi_{\text{eq}} \right) = \ldots$$

Substitution of Eq. (11) into Eq. (13) yields the following expression for $\Phi_{\text{eq}}$:

$$\ln \left( \Phi_{\text{eq}} \right) = 1 - \frac{\gamma (1+\gamma/8) \theta}{(1-\theta)} - (\gamma^2/8-1) \ln(1-\theta) - Z(\theta).$$

This is a convenient, and hopefully accurate, semiempirical expression for the adsorption probability for equilibrium.
systems (in random adsorption processes, the adsorption probability is equal to the averaged ASF).

Figures 8 and 9 compare $\Phi^{\text{EQ}}$, as calculated from Eq. (14), with $\Phi^{\text{RSA}}$ from simulation for aspect ratios 2, 6, and 15. The adsorption probability in the equilibrium case is, in general, greater than that for RSA. Both curves eventually fall to zero, although at very different coverages. Surface diffusion permits equilibrium configurations to reach much higher densities than RSA configurations. Diffusion also creates space for adsorbing particles thus accounting for the increased adsorption probability. For the short particles ($\alpha=2$), the maximum deviation between $\Phi^{\text{EQ}}$ and $\Phi^{\text{RSA}}$ occurs at approximately 65% of the RSA jamming coverage. As the elongation increases, the maximum deviation occurs earlier in the RSA coverage range: 40% of the jamming coverage for $\alpha=6$ and 25% for $\alpha=15$.

In the study by Cuesta and Frenkel, the orientational ordering transition of two-dimensional hard-ellipse systems is investigated. They report that as the coverage increases, the system undergoes an isotropic-to-nematic phase transition at a coverage which depends upon particle elongation. Their simulation results show no transition for

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**FIG. 8.** Comparison of $\Phi^{\text{RSA}}$ with $\Phi^{\text{EQ}}$ for ellipses with aspect ratio $\alpha=2$, 6, and 15.

**FIG. 9.** Comparison of $\Phi^{\text{RSA}}$ with $\Phi^{\text{EQ}}$ for spherocylinders with aspect ratio $\alpha=2$, 6, and 15.
\( \alpha = 2 \), a first-order transition for \( \alpha = 4 \) at a coverage \( \theta \approx 0.74 \), and a continuous transition for \( \alpha = 6 \) at \( \theta \approx 0.59 \). As particle length is increased, the equilibrium surface phase becomes orientationally ordered at even lower coverages. There is no existing data concerning the transition for \( \alpha > 6 \). RSA systems, on the other hand, are unable to order as such because of the immobility of particles on the surface. As pointed out in Paper I, the RSA saturation coverage displays a maximum and decreases as \( \alpha \) becomes very large. It is possible, however, that even though the RSA jamming coverage for anisotropic particles decreases with increased elongations, the coverage at which the orientational ordering transition takes place for equilibrium surfaces may decrease even faster with particle elongation. If this were true, the ordering transition could occur within the RSA coverage range. At a given coverage, the equilibrium surface configuration would be much more ordered which would increase the adsorption probability markedly over that of RSA. Additional simulation studies are required to investigate this idea.

V. CONCLUSIONS

In this paper we have analyzed the low-to-intermediate coverage kinetics of the RSA of nonspherical particles. The coefficients of the series expansion which describes the adsorption kinetics at low coverage are calculated to third order and the resulting expansion is compared to simulation data for rectangles, ellipses, spherocylinders, and needles. These comparisons reveal the shrinkage of the low-coverage regime with particle elongation due to the increased significance of the intermediate needlelike regime discussed in Paper I. In addition, it is shown that the third-order expansion diverges from the simulation curve at a lower coverage than does the second-order expansion for \( \alpha = 4 \). Interpolation formulas for \( \Phi_{\text{RSA}} \), which combine the form of the kinetics in both the low- and high-coverage regimes, show satisfactory agreement with simulation data over the entire range of coverage for all of the elongations and geometries studied. However, they fail to predict the maximum in the saturation coverage vs particle elongation. Consistently low estimates of the jamming limit for \( \alpha > 4 \) are attributed to the reduction of the low-coverage regime as the intermediate needlelike regime becomes significant. We have compared RSA simulation data to an expression for the averaged ASF obtained from an equation of state for the surface phase. The averaged ASF, or adsorption probability, at a given coverage is smaller in RSA than that for systems with surface equilibrium over the entire range of coverage. Diffusion on the surface in the equilibrium case permits longer-range orientational ordering which increases the available space for adsorbing particles and hence the adsorption probability.

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