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LETTER TO THE EDITOR

Random sequential adsorption of polydisperse mixtures: asymptotic kinetics and structure

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Abstract. We study the asymptotic kinetics of the random sequential adsorption (RSA) of a mixture of particles with a continuous distribution of sizes. Our results provide further support for the idea that the power law exponent for the approach to the jamming limit is simply related to the number of degrees of freedom of the adsorbing species. We also predict the behaviour of the mean radial distribution function in the asymptotic regime.

It is easy to understand why the random sequential adsorption (RSA) model has received much recent attention [1–11]. Although the defining algorithm for this irreversible process (the sequential placement of objects at random on a surface without overlap or diffusion of the objects once placed) is simple, the resulting behaviour is complex. Simulation studies, particularly of non-spherical particles, require considerable computational resources which were not available when the model was first proposed [12, 13]. Moreover, apart from its intrinsic interest, RSA is thought to be applicable to a wide variety of physical, chemical and biological processes. A number of related models have also been studied recently [14–17].

A unique and fascinating aspect of the RSA process, which has captured much of the research effort, is the asymptotic approach to the saturation coverage. It was first conjectured by Feder [18] and later proved by Swendsen [19] and Pomeau [20], that for spherical particles in d dimensions the density approaches its saturation value according to the power law

$$\rho(\infty)-\rho(t)\sim t^{-1/d}. \tag{1}$$

Although Swendsen argued that the same law should apply quite generally to all objects [19], we recently presented numerical and theoretical arguments that indicate otherwise [3]. For weakly elongated ellipses the correct power law appears to be

$$\rho(\infty)-\rho(t)\sim t^{-p} \tag{2}$$

with $p=\frac{1}{3}$. Other studies appear to confirm this result for weakly elongated ellipses [8] and rectangles [9], and a careful numerical study of unoriented squares unambiguously found $p=\frac{1}{3}$ [6]. It is unclear how to extend the analytical argument to more elongated particles, since the target areas no longer have a simple geometry. Moreover, the numerical determination of the power law exponent is particularly difficult for highly elongated particles. It has been suggested that the exponent p is the inverse of the

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number of degrees of freedom of the adsorbing species [6], so that $p \approx \frac{1}{3}$ for any two-dimensional anisotropic body. However, this must remain a conjecture until more definitive simulation data become available.

In this letter we present an analysis for the asymptotic kinetics of the RSA of a mixture of spherical particles with a continuous distribution of sizes. This extension of the RSA theory is not only of academic interest since in many of the physical applications the adsorbing particles are indeed polydisperse (e.g. the adsorption of latex spheres on silica). Previously, we studied a two-component mixture of hard disks of greatly differing diameter adsorbing on a planar surface [4]. While the large disks approach their saturation coverage exponentially, the smaller disks follow the usual power law, (1) ($d=2$). However, the properties of a continuous mixture are quite different. For simplicity, we specialize our analysis to two dimensions, although it is easy to generalize the results to arbitrary dimension. At zero coverage, the adsorption probability per unit time for a disk of diameter σ is $K(\sigma)$, which we assume is continuous for $\sigma_1 \leqslant \sigma \leqslant \sigma_2$, and zero for σ outside this range. In general, this is related to the bulk concentration $c(\sigma)$ by $K(\sigma)=K_0(\sigma)c(\sigma)$, where $K_0(\sigma)$ depends on the details of the interaction between the surface and an isolated particle of diameter σ. Here we consider only the case for which $\sigma_1>0$. The onset of the asymptotic regime in a monocomponent system (i.e. $K(\sigma)=k\delta(\sigma-\sigma_1)$) occurs when the available surface, i.e. that area which can be occupied by a new particle without resulting in an overlap with previously adsorbed particles, consists of isolated target areas each of which can be occupied by the centre of one and only one additional disk. For a polydisperse mixture we define a time t_c, at which point there exist only isolated targets that can accommodate the centre of only one additional disk for *all* σ. Of course many targets, perhaps the majority, do not exist for the full range of σ, but only for σ close enough to the smallest diameter, σ_1.

Each target is characterized by a length h which is a function of the diameter of the incoming particle. We assume that h, for σ close enough to σ_1, is an analytic function of $(\sigma-\sigma_1)$ and that $h(h_1,\sigma)\approx h_1-\lambda(\sigma-\sigma_1)$ for $h_1 \geqslant \lambda(\sigma-\sigma_1)\geqslant 0$ and is zero otherwise; h_1 is the characteristic length of the target for an incoming particle of diameter σ_1 and λ is a constant >0 (figure 1). In one dimension, λ is equal to 1; in 2 or more dimensions, there exists a distribution of λ's related to the details of the target

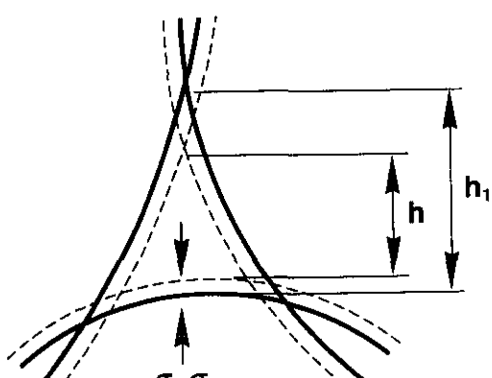

Figure 1. Illustration of a target area. The solid lines form the target for the centre of an incoming particle of diameter σ_1 (the smallest possible), while the dashed lines show the smaller target which is accessible to a particle of diameter σ ($>\sigma_1$).

shapes, but all λ's are >0 and it is sufficient, in order to determine the asymptotic behaviour, to consider a constant (mean) value λ. The asymptotic kinetics are determined by the rate at which the targets are occupied. If $n(h_1;\, t)\, \mathrm{d}h_1$ is the number of targets with a scale parameter between h_1 and $h_1 + \mathrm{d}h_1$ at time t, then the total number of additional particles (per unit area) that will be adsorbed if the process is allowed to go to completion is

$$\rho(\infty) - \rho(t) = \int_0^{H_1} \mathrm{d}h_1\, n(h_1;\, t) \tag{3}$$

where H_1 is an upper cutoff length. The probability that a target is occupied by a particle of diameter σ is proportional to $K(\sigma)h(h_1, \sigma)^2$. Hence

$$\frac{\mathrm{d}}{\mathrm{d}t} n(h_1;\, t) = -\left[\int_{\sigma_1}^{\sigma_1 + h_1/\lambda} \mathrm{d}\sigma\, K(\sigma) h(h_1, \sigma)^2\right] n(h_1;\, t) \tag{4}$$

the solution of which is

$$n(h_1;\, t) = n(h_1;\, t_c) \exp\left[-\frac{h_1^3}{\lambda} \int_0^1 \mathrm{d}\alpha\, K\left(\sigma_1 + \frac{h_1}{\lambda}(1-\alpha)\right) \alpha^2 (t - t_c)\right]. \tag{5}$$

The leading term in the asymptotic regime is determined by the smallest targets. Therefore, $n(h_1;\, t_c) = n(0;\, t_c) + \mathrm{O}(h_1)$ with $n(0;\, t_c) \neq 0$. Using this result and substituting (5) in (3) we have

$$\rho(\infty) - \rho(t) \sim n(0;\, t_c) \int_0^{H_1} \mathrm{d}h_1 \exp\left[-\frac{h_1^3}{\lambda} \int_0^1 \mathrm{d}\alpha\, K\left(\sigma_1 + \frac{h_1}{\lambda}(1-\alpha)\right) \alpha^2 \tau\right] \tag{6}$$

where $\tau = t - t_c$. We now consider two cases:

(i) if $K(\sigma_1)$ is different from zero then $K(\sigma_1 + (1-\alpha)h_1/\lambda) = K(\sigma_1) + \mathrm{O}(h_1)$. Replacing the upper limit of the integral with infinity, which does not modify the leading contribution, we find

$$\rho(\infty) - \rho(t) \sim t^{-1/3} \tag{7}$$

(ii) If $K(\sigma_1) = 0$ and $K^{(1)}(\sigma_1) = \ldots = K^{(n-1)}(\sigma_1) = 0$, $K^{(n)}(\sigma_1) > 0$, and $K^{(n)}(\sigma)$ is continuous in the vicinity of σ_1, then we find

$$\rho(\infty) - \rho(t) \sim t^{-1/(3+n)}. \tag{8}$$

Equations (7) and (8) are, then, the asymptotic power laws for the approach of the average density to its jamming limit value.

The result (7) is certainly consistent with the hypothesis concerning the number of degrees of freedom—in this case two translational, plus one corresponding to the continuous distribution of particle diameters. In d dimensions we predict an exponent of $p = 1/(d+1)$. A physical interpretation is less obvious for (8), although increasing n implies a greater degree of polydispersity around σ_1. Generalizing the above treatment, we anticipate $p = 1/(d+1+n)$ in d dimensions.

We can also inquire about $\rho_\sigma(t)\, \mathrm{d}\sigma$, the number density of disks of diameter $\varepsilon[\sigma, \sigma + \mathrm{d}\sigma[$ at time t. For $\sigma_c \geqslant \sigma > \sigma_1$ where σ_c is an upper cutoff diameter smaller than σ_2, we have that

$$\rho_\sigma(\infty) - \rho_\sigma(t) \sim \int_{\lambda(\sigma - \sigma_1)}^{H_1} \mathrm{d}h_1\, n(h_1;\, t) P(\sigma, h_1) \tag{9}$$

where

$$P(\sigma, h_1)\, \mathrm{d}\sigma = \frac{K(\sigma) h(h_1, \sigma)^2}{\int_{\sigma_1}^{\sigma + h_1/\kappa} \mathrm{d}\sigma\, K(\sigma) h(h_1, \sigma)^2}\, \mathrm{d}\sigma \tag{10}$$

is the probability that a target characterized by h_1 is occupied by a disk of diameter $\varepsilon[\sigma, \sigma+\mathrm{d}\sigma[$ and $h(h_1, \sigma) = h_1 - \lambda(\sigma+\sigma_1)$. Inserting the solution for $n(h_1; t)$ and with the assumed behaviour of $n(h_1; t_c)$ and $K(\sigma_1)$ (case (i) above) we find that

$$\rho_\sigma(\infty) - \rho_\sigma(t) \underset{t\to\infty}{\sim} \frac{\exp(-\frac{1}{3}A(\sigma)t)}{(A(\sigma)t)^3} \tag{11}$$

where $A(\sigma) = K(\sigma_1)\lambda^2(\sigma-\sigma_1)^3$. It is important to emphasize that (11) is valid only for $\sigma > \sigma_1$. Now the previous result, (8), should be recoverable from

$$\rho(\infty) - \rho(t) \simeq \int_{\sigma_1}^{\sigma_c} \mathrm{d}\sigma(\rho_\sigma(\rho_\sigma(\infty) - \rho_\sigma(t)). \tag{12}$$

However, by substituting (11) in (12) one obtains an infinite coefficient for the $t^{-1/3}$ term. One must be careful in taking the integration over σ and the limit $t \to \infty$ in the proper order. This can be achieved by starting from (9). Similarly it can also be shown that the surface coverage $\Theta(t)$ evolves as

$$\Theta(\infty) - \Theta(t) \sim \int_{\sigma_1}^{\sigma_c} \mathrm{d}\sigma\, \sigma^2(\rho_\sigma(\infty) - \rho_\sigma(t)) \underset{t\to\infty}{\sim} t^{-1/3}. \tag{13}$$

An interesting structural characteristic of monodisperse RSA configurations in the asymptotic regime is the existence of a logarithmic divergence in the radial distribution function at contact, i.e. $g(r) \sim -\ln(r/\sigma+1)$ [1, 18, 19]. This behaviour, which is unique to the RSA process, results from the immobility of the adsorbed disks and the existence of targets in the asymptotic regime. We may describe the polydisperse RSA configuration with $g(r; \sigma, \sigma'; t)$, the partial radial distribution function: $\rho\sigma'(t)g(r; \sigma, \sigma'; t)\,\mathrm{d}r\,\mathrm{d}\sigma\,\mathrm{d}\sigma'$ is the density of particles with a diameter between σ' and $\sigma'+\mathrm{d}\sigma'$ whose centre is at a distance between r and $r+\mathrm{d}r$ from the centre of a given particle with a diameter between σ and $\sigma+\mathrm{d}\sigma$. Less information is contained in the mean radial distribution function, $g(r; t)$, the normalized pair correlation function for disk centres regardless of their diameters, which is defined as

$$\rho(t)^2 g(r; t) = \int_{\sigma_1}^{\sigma_2} \mathrm{d}\sigma \int_{\sigma_1}^{\sigma_2} \mathrm{d}\sigma'\, \rho_\sigma(t)\rho_{\sigma'}(t) g(r; \sigma, \sigma'; t). \tag{14}$$

To determine the asymptotic behaviour of these functions it is necessary not only to assume that the target size scales as $h = h_1 - \lambda(\sigma-\sigma_1)$, but also that the target is formed by three surrounding particles. These triangular targets have been observed in computer simulations of monocomponent RSA configurations, and their existence in the polydisperse mixture seems reasonable, certainly if the range of particle diameters is narrow enough. Following the analysis developed for the monocomponent system [1], we find that $g(r; \sigma; \sigma'; t)$ can be written as the sum of two parts; a regular part which is certain to contain no diverging terms and a potentially diverging term. In particular,

$$g\left(\frac{\sigma+\sigma'}{2} + z; \sigma; \sigma'; t\to\infty\right) \sim \frac{1}{z+\lambda(\sigma-\sigma_1)} + \frac{1}{z+\lambda(\sigma'-\sigma_1)} + \text{regular part}. \tag{15}$$

Using the property that $g(r; \sigma, \sigma'; t) = 0$ for $r < (\sigma+\sigma')/2$ and (14), one finds that for finite time

$$g(\sigma_1+\varepsilon; t) \underset{\varepsilon\to 0^+}{\sim} \varepsilon^2 \tag{16}$$

while in the infinite time limit one finds, with the help of (15), that

$$g(\sigma_1+\varepsilon;\, t\to\infty) \underset{\varepsilon\to 0^+}{\sim} \varepsilon. \tag{17}$$

Thus no logarithmic divergence is found for the mean radial distribution function in the jamming limit. The results are independent of the dimensionality and the form of $K(\sigma)$, i.e. whether case (i) or (ii) provided that $K(\sigma)$ is continuous in the vicinity of σ_1.

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