Filling of the one-dimensional lattice by *k*-mers proceeds via fast power-law-like kinetics

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During the filling of a one-dimensional lattice by *k*-site-long hard particles, we find that after initial "jamming" a power-law-like decay of the density of interparticle gaps occurs, described by a much larger exponent than that expected from mean-field theory. We show that this effect dominates post-jamming filling for large *k* and should be observable, e.g., during the binding of proteins along a long, stretched DNA molecule.

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Problems related to adsorption and desorption of particles along a one-dimensional (1D) track are central to biological and soft-matter physics. Binding and unbinding of kinesin motors to microtubules [1], of myosins to actin filaments, and of proteins to DNA are heavily studied biological examples. For this one-dimensional situation the self-organization kinetics are surprisingly complex, displaying jamming and slow relaxation [1–4].

For irreversible adsorption (no desorption), particles with excluded volume randomly added to a line quickly reach a "jammed" configuration where no more particles can be added. In the simplest version of this "random sequential adsorption" (RSA) process, jamming occurs when about 75% of the line is filled; the approach to this jammed state is known to be exponential in time [5]. In this case, thermal equilibrium (a fully filled line) cannot be reached [5,6]. Including diffusion allows reorganizations that allow the line to entirely fill with particles [7]. However, in any chemically reversible situation, there is some finite rate of particle dissociation, causing the particles to reach a finite-temperature equilibrium density below complete filling. We report that over densities from jamming up to near-filling, desorption-mediated filling of a 1D lattice by *k*-site-long particles proceeds via a power-law-like evolution, described by an exponent much larger than that expected from mean-field theory (MFT) [8].

We consider identical rods of unit length, interacting only via mutual exclusion, adsorbing onto a line of length L ($L \gg 1$) at rate r_{on} (the unit rod length removes length dependence from r_{on} giving it dimensions of 1/time). The adsorbed rods can either desorb at rate r_{off}, or possibly diffuse along the line with a rate r_{d} [Fig. 1(a); note r_{d} has dimensions of 1/time]. The hard cores occupy k consecutive sites along a discrete lattice (lattice size $a=1/k$); as $k\to\infty$ one obtains the continuum Tonks gas limit [9].

For these models (specified by k, r_{on}, r_{off} and r_{d}), the number density of particles ρ will evolve with time t. We focus on time evolution of the "gap density" $y=1-\rho$ starting from a completely empty state at $t=0$. Qualitatively, y will show some initial rapid filling kinetics, and possibly a regime of RSA-like jamming. Then, given some combination of diffusion or desorption, y will equilibrate. Only when there is nonzero r_{off} can thermal equilibrium with density below complete filling be reached.

A version of this model which has been heavily studied is the case of no desorption, but with diffusion ($r_{\mathrm{on}}>0$, $r_{\mathrm{off}}=0$ and $r_d>0$). Given sufficiently large r_{on}, particles rapidly bind, and RSA-like jamming occurs. However, particle diffusion eventually opens large enough gaps to allow more particles to bind, and as $t\to\infty$ the line is completely filled ($y\to 0$). The approach to complete filling occurs via power-law kinetics for all finite k [10]. For $k>3$, MFT is valid, and provides the power law $y(t)\sim t^{-1/(k-1)}$ observed in numerical studies [8]. MFT considers diffusion of single-site gaps or "holes" between cores. Ignoring hole-hole correlations, and noting that k holes must coalesce to permit one more particle to bind leads to $dy/dt\propto -y^k$, and thus the MFT exponent. In the continuum limit $k\to\infty$ this exponent goes to zero; more precise studies of the continuum adsorption-diffusion model [7] verify that it displays logarithmic relaxation $y(t)\equiv 1-\rho(t)\sim 1/\ln[t\ln(t)]$.

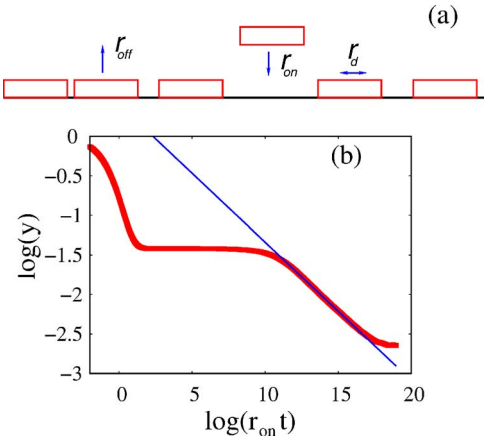

FIG. 1. (Color online) (a) Shown are adsorption(on), desorption-(off), and diffusion events. (b) The gap density versus time for $k=20$; $r_{\mathrm{off}}/r_{\mathrm{on}}=10^{-5}$, $r_{\mathrm{d}}=0$, and $L=20\times 10^5$ lattice sites. Four regimes are observed: a rapid initial filling, jamming (constant y), an ordering regime with power-law-like decay of y, and an exponential decay to the equilibrium. The straight line with a slope ≈ 0.175 is a guide to the eye, showing that the decay is much faster than the expected late time exponent $z=1/19$.

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Here, we consider the complementary case of rapid adsorption and slow desorption but no particle diffusion ($r_{off}/r_{on} \ll 1$, $r_d=0$). This is relevant to the slow reorganization of relatively strongly binding molecules along a 1D track, where the final state will be nearly filled [in the weak-binding case, $r_{off}/r_{on} \leqslant 1$, there is then a low final bound density with no jamming inhibiting equilibration [4]; we do not consider this case in this paper]. Starting with zero density at $t=0$, after times $\approx 1/r_{on}$ the line rapidly fills with particles, approaching the RSA jamming density at time $t \approx 3/r_{on}$. Nothing more can happen until desorption begins to play a role, at later times $>1/r_{off}$. On this longer time scale, desorption can open large enough gaps for additional adsorptions and equilibration to occur. Our interest is in the time evolution in this later, post-jamming time range $t>1/r_{off}$, which has not been studied for $2<k<\infty$.

Success of MFT for the large-k adsorption-diffusion model (recall MFT gives correct scaling behavior for $k>3$) has prompted similar theories for the adsorption-desorption model. For the continuum limit ($k\to\infty$) and small r_{off}, MFT predicts that density approaches equilibrium logarithmically [11,12]. Other authors have suggested that the continuum model displays "glassy" relaxation [3]. A careful study of the $k=2$ discrete adsorption-desorption model by Frey and Vilfan [1] revealed power-law density relaxation $y \sim t^{-z}$ with $z=0.5$; those authors argued that the exponent is exactly $z=1/2$, equal to that for the diffusion-dominated kinetics. Frey and Vilfan suggested that for larger k the desorption exponent might conincide with that for diffusion-relaxation, i.e., $z(k)=1/(k-1)$, with logarithmic relaxation in the continuum limit, but this suggestion was not further examined.

This unsettled situation motivated us to examine the filling kinetics for the k-mer models with slow desorption. The presence of two widely separated timescales ($1/r_{on} \ll 1/r_{off}$) and the necessity to evolve large ($\approx 10^5$ particle) systems from zero density to equilibrium led us to use the Gillespie algorithm [13] where the time to the next on- or off-event is computed stochastically at each step of the simulation.

In the k-mer model the ratio of the rates r_{on} and r_{off} is simply related to the equilibrium density. The total rate of adsorption is proportional to the length available on the line such that a particle can be adsorbed satisfying the hard-core constraint

$$\Gamma_{on} = r_{on}\rho \frac{\sum_{m=k}^{\infty} (m-k+1)g(k,m)}{\sum_{m=0}^{\infty} g(k,m)} \qquad (1)$$

where ρ is the density of the particles on the line and $g(k,m)$ is the gap distribution (the number of m-lattice-site gaps). The total rate of particle desorptions is simply proportional to the number of rods on the line: $\Gamma_{off}=r_{off}\rho$. In equilibrium, $\Gamma_{on}=\Gamma_{off}$, giving:

$$\frac{r_{off}}{r_{on}} = \left(\frac{1-\rho_{eq}+\rho_{eq}/k}{\rho_{eq}}\right)\left(\frac{1-\rho_{eq}}{1-\rho_{eq}+\rho_{eq}/k}\right)^k. \qquad (2)$$

As expected, $\bar{r}_{off}/r_{on} \to 0$ as $\rho \to 1$. The right-hand side of (2) is simply $e^{-\mu}$, where μ is the chemical potential of the k-mer gas (in units of k_BT).

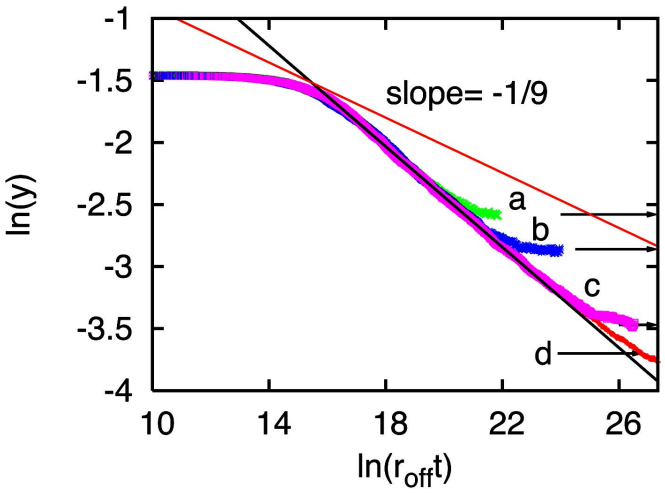

FIG. 2. (Color online) The gap density decay in adsorption-desorption mediated filling of 10 mers on a lattice for r_{off}/r_{on} values (a, green) 10^{-4}, (b, blue) 10^{-5}, (c, pink) 10^{-7}, and (d, red) 10^{-10}, with an apparent exponent 0.2. The power-law-like decay persists up to a density $\rho \approx 95\%$. A line with a slope $=-1/9$, corresponding to the expected late time mean-field exponent, is plotted to demonstrate the far faster decay of the gap density. Note that even at a filling of $\approx 98\%$, the decay is faster than $-1/9$. The arrows at the right indicate the corresponding equilibrium densities. The straight line (black) with a slope $=-0.2$ is a guide to the eye.

We have computed the gap density for k mers on a lattice for different values of k. For dimers ($k=2$), we recover the results of Frey and Vilfan [1], i.e., a power-law equilibration with an exponent $z=0.5$. Interestingly, this is same as the exponent for the case with adsorption and diffusion (without desorption) for dimers [14]. However, we find that for larger values of k, the apparent exponents in the adsorption-desorption model deviate from the late time adsorption-diffusion exponent expected from MFT. Figure 1(b) shows a plot of gap density versus time for $k=20$; $r_{off}/r_{on}=10^{-5}$, $r_d=0$, and $L=20\times 10^5 a$. At $t=0$, the line is empty, so the gap density $y(t=0)=1$. Then, y shows four stages of time evolution. In the first stage y decreases rapidly, corresponding to random adsorptions. As discussed earlier, this leads to jamming at a time $\ln(r_{on}t) \approx 1$, at the RSA gap density $y \simeq 0.76$. The system then stays in the jammed state for a time $\approx 1/r_{off}$, or until $\ln(r_{on}t) \approx 10$. Then, desorption events take place, and the gap density follows an apparent power-law decay over the time range $\ln(r_{on}t) \approx 11$ to 16; over this range a power-law fit gives $y \sim t^{-0.1747\pm 0.0002}$. Finally the system relaxes exponentially to equilibrium [y reaches the value given by Eq. (2)]. Surprisingly, the post-jamming decay apparently follows a power law, but one which is far faster than the expected $y \sim t^{-1/19}$ [1,7].

We studied the dynamics for different values of r_{off}/r_{on} ratios. Figure 2 shows the gap density decay for ten-mers. The post-jamming power-law-like behavior with $z=0.2$ extends up to a very high density $\approx 95\%$, spanning more than 3 decades in time. Again, the apparent exponent is far above the expected MFT exponent (1/9). As r_{off}/r_{on} is reduced, the equilibration time increases as expected, but does not reveal a regime where the MFT exponent can be observed. Similar

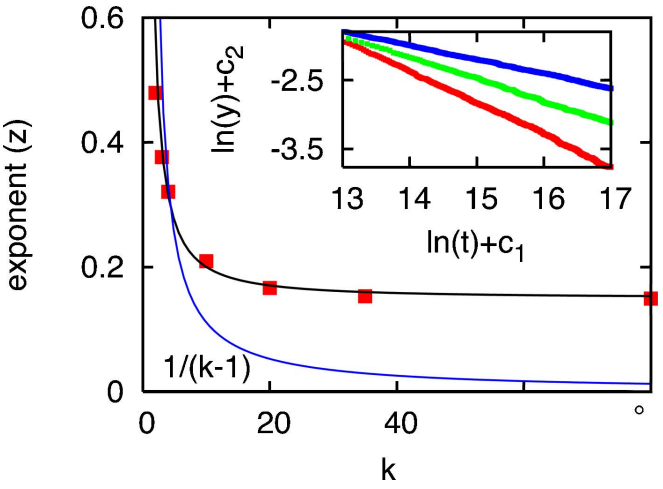

FIG. 3. (Color online) The adsorption and desorption of k mers on a lattice: the apparent power-law exponents for gap density decay, observed soon after jamming, as a function of k (filled squares). As $k\to\infty$ the exponent goes to 0.15. The line passing through the filled squares is a guide to the eye. Note that the adsorption-desorption exponents are above the mean-field adsorption-diffusion result $z(k)=1/(k-1)$, for all $k>4$. Inset shows the power-law regime in the $y(t)$ for $k=2$ (red), 4 (green), and 10 (blue).

calculations for $2<k<35$ revealed power-law-like decays; the resulting exponents are plotted in Fig. 3 (points). The apparent exponents are well above the expected MFT exponents (curve going to zero as $k\to\infty$) for all $k>4$. The inset of Fig. 3 shows post-jamming power-law decays of y for $k=2$, 4, and 10.

Figure 4 shows a gap density as a function of time for the continuum case ($k=\infty$) for $r_{off}/r_{on}=10^{-7}$, $r_d=0$, and $L=10^5$. The gap density shows jamming, followed by an apparent power-law decay. However, as $r_{off}/r_{on}\to 0$ we observe a slowdown of the kinetics for densities above 90%, which is

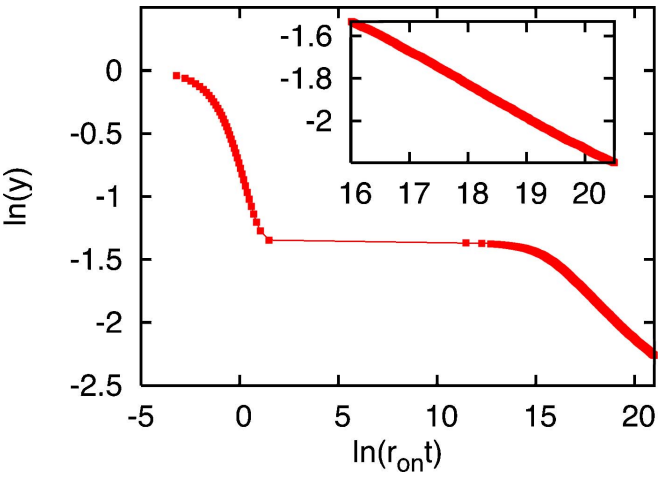

FIG. 4. (Color online) The gap density versus time for the continuum model; $r_{off}/r_{on}=10^{-7}$, $r_d=0$, and $L=10^5$. Three regimes are observed: a rapid initial filling, jamming (constant y), and an ordering regime with power-law-like decay of y. Inset: an expanded plot of apparent power-law regime; the linear fit gives the exponent $z=0.151\pm0.000\,18$.

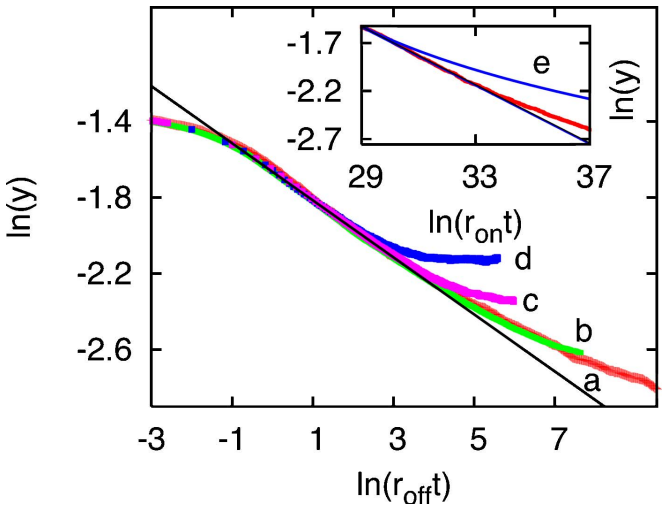

FIG. 5. (Color online) The gap density versus time for r_{off}/r_{on} = values (a, red) 10^{-13}, (b, green) 10^{-7}, (c, pink) 10^{-5}, and (d, blue) 10^{-4}. The straight line with slope=−0.15 is given to compare the decay soon after jamming. At late times (below $y\approx 0.1$), the decay follows the mean-field curve as shown in Ref. [12]. Inset: The gap density decay for $r_{off}/r_{on}=10^{-13}$ is compared with the mean-field expression [curve e, $y=1/\ln(\alpha t\ln(\alpha t))$]. α is chosen in such a way that the slope at the beginning matches. The straight line is a fit to the first power-law regime (slope=−0.15).

well described by the logarithmic decay predicted by Ref. [12] (see Fig. 5). We also observe the expected exponential approach to equilibrium [15]. Thus, our calculations recover previously known results for the continuum case.

Given that the theory of Ref. [12] describes the continuum limit, we generalized it for the k-mer model. In the limit $r_{off}/r_{on}\to 0$, the gap density is predicted to follow

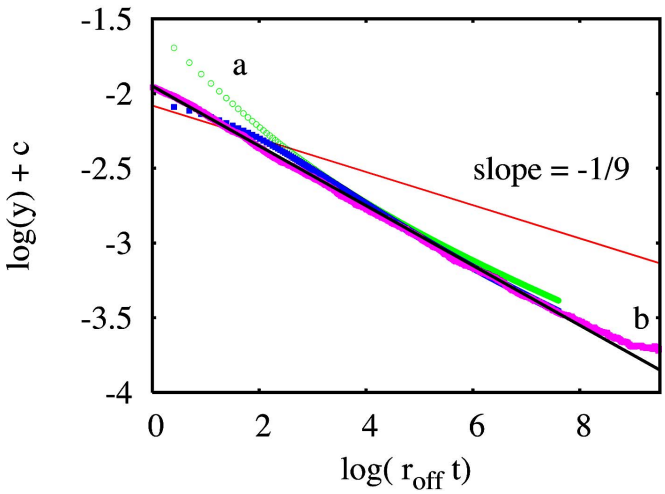

FIG. 6. (Color online) The gap density dynamics of 10-mer. Numerical solution of Eq. (3) (a, green open circles) and the mean-field equation from Ref [7] (blue filled squares) are plotted for k=10. This is compared with the Monte Carlo simulations result (b, pink). In the regime shown, all these results show a decay which is faster than the expected late time power-law decay $y\sim t^{-1/9}$ (thin red straight line). The thicker black straight line has a slope =−0.2. Curves have been shifted to line up vertically.

$$\frac{dy}{dt} \simeq -2\left(\frac{y}{y+(1-y)/k}\right)^k. \quad (3)$$

This indicates that the terminal MFT power law ($y \sim t^{-1/(k-1)}$) will only appear when $y \ll 1/(k+1)$. Thus, for large k, the terminal power law will be observed only for densities very close to complete filling; for nonzero r_{off}, the equilibrium density may well be below the level that must be reached to observe the terminal decay. Furthermore, numerical integration of Eq. (3) shows a faster decay, closely matching our simulation result (Fig. 6). The origin of this acceleration effect is the presence of an appreciable density of gaps larger than one lattice site in size. The MFT exponent $z=1/(k-1)$ is based on coalescence of single-site gaps [8], and thus requires a gap density y much below $\approx 1/k$ to ensure that most gaps are only one lattice site wide.

A gap density $y < 1/(k+1)$, small enough to permit observation of the MFT exponent, requires $r_{\mathrm{off}}/r_{\mathrm{on}} \to 0$ and $t \to \infty$. In fact we have been unable to observe the MFT exponent in any of our large finite-k calculations, and we anticipate that virtually any experiment would be similarly unable to observe the MFT exponent. Instead, an apparently faster power-law behavior is likely to be observed for densities between jamming and equilibrium, which we have found to be produced qualitatively, by the generalization of the theory of Ref. [12] to the discrete case (see Fig. 6).

In any realistic situation, adsorption, desorption, and diffusion should all occur at nonzero rates. Preliminary results for the continuum model with $0 < r_{\mathrm{off}} \approx r_{\mathrm{d}} \ll r_{\mathrm{on}}$ (setting the particles to unit length gives r_{d} dimensions of 1/time) indicate the same equilibration kinetics as for $r_{\mathrm{d}}=0$. We have also studied adsorption-desorption dynamics introducing cooperativity, i.e., including an attractive interparticle potential with a finite range. One can incorporate these interactions either with the on-rate or off-rate, while maintaining the same Boltzmann equilibrium. When the attractive interactions are predominantly incorporated into the on-rate, we have "polymerization," or adsorption of successive adjacent particles, and the density increases essentially linearly with time. However, when the interactions are put predominantly into the off-rate, the gap density y follows a power-law-like equilibration similar to that discussed here, but with a larger apparent exponent ≈ 0.2 independent on the strength of the cooperative interaction.

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