Comment on "Kinetics of Random Sequential Adsorption"

Recently Schaaf and Talbot (ST)[1] derived an exact expansion in coverage, Θ, for the rate of random sequential adsorption (RSA) of disks on the plane. Here we present a simpler derivation, analogous to that used for lattice RSA processes.[2] We also show how to resum such expansions to provide remarkably accurate estimates of saturation or jamming coverages, Θ_s. We note that RSA problems can also be treated by approximation truncation of exact hierarchial rate equations.[3]

Let N denote the number density of disks of radius R which have adsorbed at a rate of 1 per unit area. Then dN/dt equals the probability, $\odot$, that no disks have centers within the "exclusion disk" of radius $\sigma = 2R$ centered on the point of adsorption. Now $d\odot/dt$ involves an integral over probabilities of larger empty configurations required for adsorption onto $\odot$. Continuing to derive rate equations for these larger configuration probabilities produces an infinite hierarchy (Fig. 1). Initial values of higher derivatives of N or dN/dt are simply given by (multiple) integrals over areas which appear on the right-hand side (RHS), and so

$$\frac{dN}{dt} = 1 - \pi\sigma^2 t + \tfrac{1}{2}\int_{|R|<\sigma} dR\, q_2(R) t^2 + \cdots , \quad (1)$$

using ST notation. Inverting the corresponding expansion for $\Theta = \pi R^2 N$ and substituting into (1) nontrivially recovers the ST results.

From analogous hierarchies for lattice RSA processes (Fig. 1), initial values of higher derivatives of Θ or $d\Theta/dt$ are obtained by simply counting the number of terms appearing on the RHS.[2] One can then eliminate t in favor of Θ in the $d\Theta/dt$ expansions, as above. For random filling of lattice sites with no filled nearest neighbors (NN) one has $d\Theta/dt = P_z$, where $P_z = 1 + \sum_i \geq 1 a_i \Theta^i$ is the probability of an empty site with all z NN empty. For hexagonal ($z=3$), square ($z=4$), and triangular ($z=6$) lattices, we obtain $a_1 = -4, -5$, and -7; $a_2 = 3, 6$, and 9; $a_3 = 1, \tfrac{8}{3}$, and 8; $a_4 = \tfrac{3}{4}, -\tfrac{2}{3}$, and $\tfrac{21}{2}$; $a_5 = \tfrac{23}{20}, -\tfrac{20}{3}$, and $\tfrac{77}{5}$; ..., respectively. These agree with the exact z-coordinated Bethe-lattice behavior,[4]

$$P_z = [(z-1)(1-2\Theta)^{z/2} - (1-2\Theta)]/(z-2) ,$$

to order Θ^{l-2}, where l is the length of a lattice loop.

One achieves consistent acceleration in convergence of these dN/dt and P_z expansions, and improvement in associated Θ_s estimates, after resummation to incorporate exact near-Θ_s behavior. For the ST RSA problem where[5] $dN/dt \sim c(\Theta_s - \Theta)^3$, we write $dN/dt \approx (1 + b_1 X + b_2 X)(1 - X)^3$ with $X = \Theta/\Theta_s$. Determining Θ_s and b_i by matching to the ST cubic expansion yields $\Theta_s = 0.553$ (cf. 0.547 from simulation). For the lattice
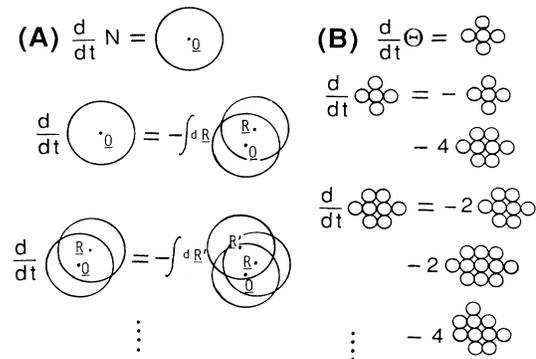
FIG. 1. Hierarchial rate equations for RSA (A) of disks on the plane, and (B) at sites on a square lattice with no filled NN sites. Probabilities of configurations of overlapping exclusions disks (free of disk centers) or of empty lattice sites are denoted by the configurations themselves. Integrals in (A) range over the configuration on the left-hand side.

RSA problems where[2] $P_z \sim \Theta_s - \Theta$, we write $P_z = (1 + b_1 X + \cdots + b_5 X^5)(1 - X)$ with $1 + b_1 + \cdots + b_5 = \Theta_s$. Determining Θ_s and b_i by matching to the quintic P_z expansions above yields $\Theta_s = 0.3759, 0.3699$, and 0.2316 for $z = 3, 4$, and 6, respectively (cf. 0.379, 0.3641, and 0.2314 from simulation). The procedures described here are general, applying to other RSA problems. For example, for the Palisti problem of random filling of nonoverlapping 2×2 squares on a square lattice, analogous resummation of the quartic expansion for the adsorption rate yields $\Theta_s = 0.7462$ [cf. $0.7476 \approx (1 - e^{-2})^2$ from simulation].[3]

J. W. Evans
Ames Laboratory and Department of Physics
Iowa State University
Ames, Iowa 50011

[1] P. Schaaf and J. Talbot, Phys. Rev. Lett. 62, 175 (1989).
[2] J. W. Evans, J. Chem. Phys. 87, 3038 (1987); Physica (Amsterdam) 123A, 297 (1984); D. K. Hoffman, J. Chem. Phys. 65, 96 (1976); A. Baram and D. Kutasov, J. Phys. A 22, L251 (1989).
[3] P. Schaaf et al., J. Phys. Chem. 92, 4826 (1988); R. S. Nord and J. W. Evans, J. Chem. Phys. 82, 2795 (1985); K. J. Vette et al., ibid. 60, 4854 (1974).
[4] J. W. Evans, J. Math. Phys. 25, 2527 (1984).
[5] R. H. Swendsen, Phys. Rev. A 24, 504 (1981).