September 1991 OUTP–91–28 S

MULTILAYER ADSORPTION WITH INCREASING LAYER COVERAGE

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PACS: 05.70.Ln, 68.10.Jy, 82.20.Wt.

ABSTRACT

Numerical Monte Carlo studies and analytical considerations are reported indicating that in certain models of multilayer irreversible surface adsorption the density may actually increase away from the substrate. This unexpected conclusion is contrary to simple intuitive considerations in formation of amorphous deposits. The behavior of the density is found to obey a universal power law. Some time dependent properties are also examined.

Recently, several experiments on colloidal particle adhesion at surfaces have reported formation of multilayer deposits[1−3] in essentially irreversible deposition processes from unstable or marginally stable colloid suspensions. Comprehensive theoretical studies of such processes are needed both to explore the scope of phenomena involved and for applications in experimental data interpretations which thus far were limited[4] to simple mean-field (rate-equation) theories. Since colloid experiments usually involve not too many layers (up to about 30), the details of the transport mechanism of particles to the surface are less important than in studies of asymptotically multiple-layer deposits, e.g., in balistic deposition or diffusion limited aggregation.[5] Thus the appropriate deposition models may be formulated[6,7] to eliminate or suppress the screening of lower layers by particles adhering in higher layers, emphasizing those correlation and dynamics effects that result from the "jamming" or blocking due to particle size and irreversibility of the deposit formation.

Generally, deposition dominated by jamming effects will result in an amorphous deposit so that the notion of "layers" in a true *continuum deposition* can be employed only as an approximate concept. However, simplified *lattice models* can reveal many general aspects of the deposition processes as well as new unexpected features. One such result is presented in this work. Indeed, a common intuition in the formation of amorphous deposits is that due to gaps in lower layers, the higher layer coverage (i.e., the deposit density) will be decreasing with the layer number (distance from the substrate). Our results suggest that in some deposition models the effects of the gaps may be just reversed: the coverage (deposit density) actually *increases* away from the wall! This unexpected behavior is first demonstrated numerically, following the definition of the model. The convergence to the limiting coverage is found to obey a universal power law. Phenomenological argument is then given supporting the assertion that the observed effect of coverage increase with the layer number is indeed due to presence of gaps in lower layers. A monolayer model simulating the gap effect is formulated and studied numerically.

Lattice models with screening eliminated by disallowing overhangs were studied recently[6] by numerical and analytical methods. The coverage was found to decrease with the layer number both in $2D$ and in $1D$, and its power-law convergence to the limiting value far from the wall was explained by random walk arguments. The model studied here is an extension of the $1D$ model with overhangs allowed[7] but only over gaps which are small enough so that screening is eliminated. Thus, we consider deposition of k-mers (i.e., objects of length k) on a $1D$ linear substrate which is modeled by a lattice of spacing 1.

The deposition attempts are distributed uniformly over the lattice sites, with a certain rate per site which will be absorbed in the definition of the time variable T. The group of k lattice sites chosen in each deposition attempt is examined to find the lowest layer, n, in which *all* these k sites are empty. If $n = 1$, then the k-mer is "deposited." However, for layers $n > 1$ the deposition is successful only if no gaps of size k or larger are covered (this restriction is imposed in order to suppress screening[7]). Thus, the deposition is always allowed if all the "supporting" k sites in the $(n-1)$st layer are filled or have only small internal gaps. However, if the leftmost site or the rightmost site, or both of them are parts of gaps of length k or larger, extending of course beyond the k-group under consideration, in layer $(n-1)$, then the deposition attempt is rejected. For the case of dimers ($k = 2$) the rule is further illustrated in Fig. 1.

Our numerical simulations were carried out for $k = 2, 3, 4, 5, 10$. Lattice sizes were 2000, with periodic boundary conditions. The results were averaged over at least 2000 different Monte Carlo runs. We measured the time dependence of the coverage $\theta_n(T)$ (fraction of occupied sites) in several layers n, up to $T = 80$, where the time scale is defined to have one deposition attempt per lattice site per unit time. The behavior of the "jamming" coverages was then analyzed for layers $n \leq 55$ since these layers were clearly "saturated" (up to statistical noise in the data) at times $T = 80$.

Let us, however, first comment on the time dependence and specifically, compare numerical results for $k = 2$ and layers $n = 1, 2$ with other studies available in the literature. These results are presented in Fig. 2. For layer 1, the deposition in our model is not affected by other layers and is therefore identical to the monolayer deposition case for which there is an exact solution.[8] Indeed, the numerical data follow the exact curve quite closely. However, the approximate self-consistent approach for layer 2, see Ref. 7, provides at best a semiqualitative description of the coverage, typical of self-consistent theories. In fact, both the short time behavior and the large-time asymptotic coverage are not reproduced correctly by the self-consistent approximation.[7]

Qualitatively, since the higher layers have to build up on top of the lower layers, the coverage *at short times* follows the conventional intuition and decreases with layer number. For example, for $k = 2$ one can establish that

$$\theta_n(T) \approx 2T^n/n! \qquad \text{for} \qquad T << 1, \tag{1}$$

which is indeed confirmed by the data. However, for the particular deposition rule considered here the coverage in layer n eventually exceeds that in layer $(n - 1)$ at larger times. For layer 2 this is shown in Fig. 2.

This unexpected behavior was found numerically for all layers $n \leq 55$ and for all k studied. The jamming coverages are shown in Fig. 3. We employed the sequence analysis methods described in Ref. 9 with some modifications appropriate for Monte Carlo data with statistical noise, which amounted to averaging over several data points for consecutive n before applying the sequence-analysis techniques. We found clear evidence of the power-law behavior

$$\theta_n(\infty) \simeq \theta_\infty(\infty) - \frac{C}{n^\phi} \ . \tag{2}$$

All the quantities in (2) depend implicitly on k. However, the power ϕ was found to be universal and approximately near $\frac{1}{3}$ for all k studied. The sequence analyses, not detailed here, suggest the range

$$\phi = 0.3 \pm 0.15, \tag{3}$$

based on the available data for $n \leq 55$.

While we cannot explain the value of the exponent ϕ or substantiate the validity of (2) beyond numerical evidence, we can offer an argument for the unexpected increase in the higher-layer coverage at jamming. Indeed, when large enough covered (by k-mers or gaps of sizes up to $k-1$) regions have formed in layer $(n-1)$, then the deposition with overhangs beyond those regions will be delayed, as illustrated in Fig. 1. Thus, there will be some preference for higher density in layer n especially near the ends of the regions occupied in layer $(n-1)$; see Fig. 1.

To test the above suggestion, we considered the following monolayer dimer-deposition model. Let L denote the lattice size ($L = 2000$ in simulations). We select randomly $\rho L/2$ dimers and make the ρL sites thus selected unavailable for deposition for times $0 \leq T \leq T_s$. Introduction of such a "sleeping time" T_s for fraction ρ of lattice sites (grouped in dimers) in monolayer deposition supposedly will model effect of disallowed overhangs over gaps of size larger than 1 in the lower layer, $(n-1)$, on the multilayer deposition in layer n provided we loosely identify $T_s \propto n$.

Indeed, examination of our multilayer data suggests that times needed to build up the nth layer coverage grow linearly with n. For instance times $T_{1/2}$ defined via

$$\theta\left(T_{1/2}\right) = \frac{1}{2}\theta_n(\infty), \tag{4}$$

grow according to

$$T_{1/2} \simeq \tau n, \tag{5}$$

where the coefficient τ is of order 1 and gradually decreases with k: our data suggests $\tau \simeq 0.88, 0.81, 0.77, 0.74, 0.65$, for $k = 2, 3, 4, 5, 10$, respectively.

After time T_s all the blocked sites are released and can be occupied in subsequent deposition attempts. For the blocked site density $\rho = 0.5$, the resulting monolayer-model coverage is shown in Fig. 4 for several "sleeping times" T_s. In Fig. 5, we plot the jamming coverages for several values of ρ, as functions of the sleeping time T_s. Guided by the anticipated approximate correspondence $T_s \propto n$, described earlier, and by relation (2), we plotted the data vs. $T_s^{-1/3}$; compare Fig. 3. Indeed, the data roughly follow straight lines although no careful analysis of the T_s-dependence was attempted due to limited number of data points collected as compared to the multilayer case.

In summary, out study illustrates an unexpected property of voids in lower layers promoting higher-density deposit formation in higher layers. A monolayer model with "sleeping sites" confirms our conjecture that this effect is due to the delay in deposition with gaps on top of the boundaries of covered regions in lower layers.

This research was partially supported by the DFG- Sonderforschungsbereich 262/D1 (Germany) and by the Science and Engineering Research Council (UK). One of the authors (V.P.) also wishes to acknowledge the hospitality of Professor K. Binder at University of Mainz and the award of a Guest Research Fellowship from The Royal Society for his sabbatical stay at Oxford.

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FIGURE CAPTIONS

Fig. 1. (a) Configuration of layers n and $(n-1)$ with shaded areas showing regions to the right covered by dimers (with possibly 1-gaps) while the regions to the left are empty; (b) deposition of a dimer (open rectangle) in layer n which is immediately possible in the configuration a; (c) deposition attempt of a dimer in layer n which can be accepted only *after* a gap was decreased to size 1 (or zero, — not shown here) by an earlier deposition of a dimer in layer $(n-1)$.

Fig. 2. Time dependence of the coverage in layers 1 and 2 for the dimer deposition. Monte Carlo results: squares and triangles for layers 1 and 2, respectively. Exact calculation of Ref. 8 for layer 1: solid line. Approximation of Ref. 7 for layer 2: dashed line. Note that the dashed line approaches the solid line from below for $T \gtrsim 4$.

Fig. 3. Jamming coverages in layers $n = 22, 23, \ldots, 55$, plotted vs. $n^{-1/3}$.

Fig. 4. Time dependence of the coverage for the monolayer deposition of dimers with initial blocking density $\rho = 0.5$, for several "sleeping times" $T_s = 1.0, 1.5, 2.0, 3.0, 5.0$. Note that the coverages follow the same curve for times $0 \leq T \leq T_s$ and have discontinous slope at $T = T_s$. The inset enlarges the region in which the coverage curves intersect. (Note that the data in this figure are numerically calculated. Continuous curves were plotted instead of points for clarity.)

Fig. 5. Jamming coverages for several blocking densities, plotted vs. $T_s^{-1/3}$.