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Simulated growth of wetting layers

Zhihua Jiang and C. Ebner
Department of Physics, Ohio State University, Columbus, Ohio 43210
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We have done Monte Carlo simulations of the growth of wetting films in two and three dimensions for the case of nonconserved order parameters using a solid-on-solid model with nearest-neighbor interactions; cases with both short-ranged and algebraic adsorbate-substrate potentials have been examined. Where applicable, the results support the predictions of Lipowsky which are based on analysis of effective interface models. They are also in general agreement with the Ising model simulations of Mon, Binder, and Landau for the particular case of three dimensions and short-ranged adsorbate-substrate interactions.

I. INTRODUCTION

Wetting phenomena, films, and interfaces have lately received considerable attention from physicists as evidenced by the larger number of recent reviews of these topics.[1-8] They are of interest both because of their importance in many natural and technological processes and because they provide basic examples of nonuniform many-particle systems. Much research has been done in the general area of equilibrium thermodynamic properties; more recently, dynamic properties, especially the question of the manner in which equilibrium is approached, have been receiving increased attention.[5] In this paper we present the results of Monte Carlo (MC) simulations designed to study the growth of an equilibrium wetting film on a smooth substrate starting from an initial configuration in which the film is completely absent. We use a solid-on-solid (SOS) model in two and three dimensions d and so have interfaces of dimension $d-1$ equal to one or two. The interaction $V(h)$ between the film and the substrate is either short ranged or varies as h^{-p}, where h is the thickness of the adsorbed film. In all cases, $V(h)$, the temperature T, and the chemical potential μ are such that there is complete wetting at equilibrium and the system is far from any wetting, prewetting, or roughening transitions. By the nature of the SOS model, our simulations are of necessity order-parameter nonconserving.

The principal goal of this work is to examine the film thickness as a function of time, $\Gamma=\Gamma(t)$. The results may be compared with the predictions of Lipowsky[9] which are based on analysis of an effective interface model with nonconserved order parameter. They can also be compared, for the particular case of $d=3$ and short ranged $V(h)$, with the recent simulations by Mon, Binder, and Landau[10] of the Ising model with single-spin-flip dynamics.

The remainder of this paper consists of Sec. II, which contains a description of the model and Monte Carlo procedures along with a summary of Lipowsky's predictions; Sec. III presents the results; and Sec. IV is a summary and discussion.

II. MODEL AND THEORETICAL PREDICTIONS

We employ a solid-on-solid model with nearest-neighbor ferromagnetic coupling $J/2$ on a $(d-1)$-dimensional square lattice lying parallel to the surface of the substrate; $d=2$ or 3. At any site i of the lattice there is a column of adsorbate atoms of height $h_i=0,1,2,\ldots$ so that h_i is the thickness of the adsorbed film at that site. The Hamiltonian is

$$H-\mu N=(J/2)\sum_{\langle i,j\rangle}|h_i-h_j|+\sum_i[V(h_i)-\mu h_i]\ , \tag{1}$$

where $V(h)$ is the adsorbate-substrate interaction energy for a column of height h and $\langle i,j\rangle$ denotes that the sum is over nearest-neighbor pairs of sites. Bulk two-phase coexistence occurs for chemical potential $\mu=0$. This value is used in all of the simulations reported here. Two types of substrate potential were employed. The first, which we call short ranged, is simply zero everywhere,

$$V(h)=0\ , \tag{2}$$

while the second is algebraic for $h>1$,

$$V(h)=\begin{cases}7.85J & \text{if } h=0\\ 4.2J/h^p & \text{if } h>0\ .\end{cases} \tag{3}$$

The specific cases of $p=1$, 2, or 3 were used extensively; p equal to 2 or 3 corresponds, respectively, to the nonretarded or retarded van der Waals interaction. Temperatures used in the simulations are, in the case of short-ranged $V(h)$, $T=0.4J/k$ and $1.0J/k$ for $d=2$ and $T=0.8J/k$ and $2.0J/k$ for $d=3$; k is the Boltzmann constant. In the case of algebraic $V(h)$, we employed $T=0.8J/k$ for $d=3$ and $T=0.5J/k$ for $d=2$. Given the potentials used here, there is complete wetting at $T>0$ in all cases. Also, for $d=3$ there is a roughening transition at a temperature [11] $0.62J/k$ which is considerably less than the lowest temperature $(0.8J/k)$ employed for simulations. Hence there are no complications arising from metastability associated with first-order layering or wetting transitions.

The standard Metropolis method was employed in the MC simulations with a change $\Delta h_i = \pm 1$ attempted in each step. Individual runs were made with from 10^5 to 3×10^5 Monte Carlo steps per site (MCS), and the number of runs N performed for any given set of parameters ranged from 30 to 300. The starting configuration was always $h_i = 0$ for all i. The size of the lattice was L^{d-1} with L of 30, 100, 200, or 400 for $d=2$ and 10, 14, 20, or 30 for $d=3$. The quantity of primary interest is the coverage Γ, defined by

$$\Gamma(t) = L^{-d+1}\sum_i h_i(t) \ . \tag{4}$$

The coverage was computed in each run at intervals of about 100 MCS and averaged over all N runs with a given set of parameters, as was the interface width,

$$w(t) = \left[L^{-d+1}\sum_i [h_i(t)-\Gamma(t)]^2 \right]^{1/2} \ . \tag{5}$$

In some cases the profile $n(z,t)$, given by

$$n(z,t) = L^{-d+1}\sum_i \theta[h_i(t)-z] \ , \tag{6}$$

where

$$\theta(x) = \begin{cases} 1 & \text{for } x \geq 0 \\ 0 & \text{for } x < 0 \end{cases} \tag{7}$$

was also accumulated and averaged over a set of runs with identical parameters.

Our results for $\Gamma(t)$ are conveniently compared with Lipowsky's[9] theory which is for the limit $L \to \infty$. Given a potential $V(h)$ in the form of Eq. (3), these predictions may be summarized as follows: First, for

$$d > d^*(p) = (3p+2)/(p+2) \ ,$$

where $d^*(p)$ is the upper critical dimension, one has a mean-field (MF) regime where the effect of $V(h)$ dominates thermal fluctuations and leads at sufficiently long times to

$$\Gamma(t) \sim t^{1/\alpha} \ , \tag{8}$$

where $\alpha = p+2$. For $d=3$, we have this regime for any $p < \infty$. In $d=2$, we have this regime for $p<2$. Second, for $d \leq d^*(p)$, one has the fluctuation (FL) regime where fluctuations dominate the effects of the potential and produce a universal exponent where $\alpha = 4/(3-d)$. For $d=2$, we are in this regime if $p \geq 2$ and so should expect $\Gamma(t) \sim t^{1/4}$ in all such cases. For $d=3$ (and $d=2$), we are in the FL regime given the short-ranged substrate potential. In this case, for $d=3$, we have $1/\alpha \to 0$ which would be consistent with, e.g., $\Gamma(t) \sim \ln t$; this behavior was reported by Mon *et al.*[10] in their simulations of the $d=3$ Ising model with short-ranged interactions.

The foregoing will not hold for arbitrarily long times in a system with finite L; in this limit, as discussed by Mon *et al.*,[10] the growth process will revert to a one-dimensional random walk on a half-space ($h \geq 0$), leading to the long-time behavior in all cases

$$\Gamma(t) \sim t^{1/2} \ . \tag{9}$$

The coverage Γ at which the crossover takes place is expected to be of order $L^{4/(\alpha-2)}$. In the work done here, t is sufficiently short that the crossover is not observed in most cases, the case of $d=3$ and short-ranged V being a notable exception; we did, however, do some simulations on small systems to verify the presence of the crossover.

III. RESULTS

We present first our results for $d=3$ and algebraic potentials. Figure 1 is a plot of $\ln\Gamma$ versus $\ln t$ for potentials with $p=1$, 2, and 3; also $T=0.8J/k$, $L=20$, and $\mu=0$. From 30 to 90 runs of length 10^5 MCS were averaged to obtain each curve. With the exception of $p=3$, all curves are fit well by straight lines of slope $1/(p+2)$, as expected in the MF regime; such lines are included in the figure to guide the eye. For $p=3$, the expected $t^{1/5}$ behavior is present for t not too large, but for the largest times, the film is growing at a rate consistent with some larger power of t. Probably this is a finite-size effect signaling the crossover to $t^{1/2}$ behavior at very long times.

The other case that we have studied in $d=3$ is the short-ranged substrate potential. Figure 2 shows $\ln\Gamma$ versus $\ln t$ for $L=14$, $T=2.0J/k$, and 3×10^5 MCS. Some 150 runs were averaged to obtain these results. If there is in fact a regime where $\Gamma \sim \ln t$, it is for $4 \leq \Gamma \leq 8$. This interval is shown in the inset to Fig. 2 which presents Γ versus $\ln t$. The range of Γ for which this behavior is present is sufficiently limited to prevent our claiming a definitive observation of it. For thicker films $\Gamma > 20$, the behavior appears to be $\Gamma \sim t^{1/2}$, as one may see by fitting a straight line to the curve in Fig. 2 at

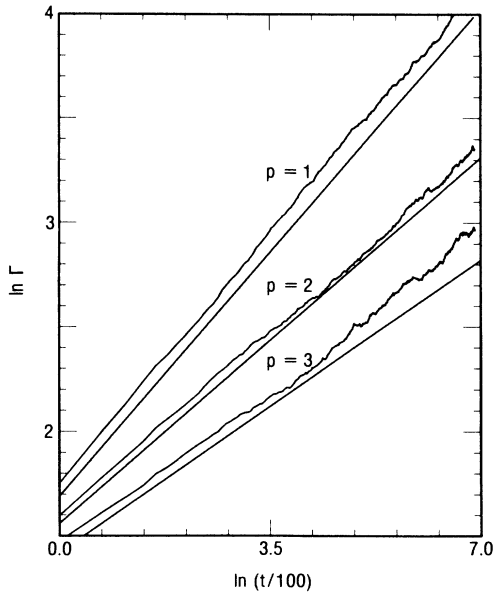

FIG. 1. The logarithm of the coverage is shown as a function of the logarithm of the time for $d=3$ and algebraic potentials with $p=1$ ($N=30$), 2 ($N=60$), and 3 ($N=90$), at $T=0.8J/k$ and with $L=20$; t is in units of 100 MCS. Lines of slope $\frac{1}{3}$, $\frac{1}{4}$, and $\frac{1}{5}$ are also shown.

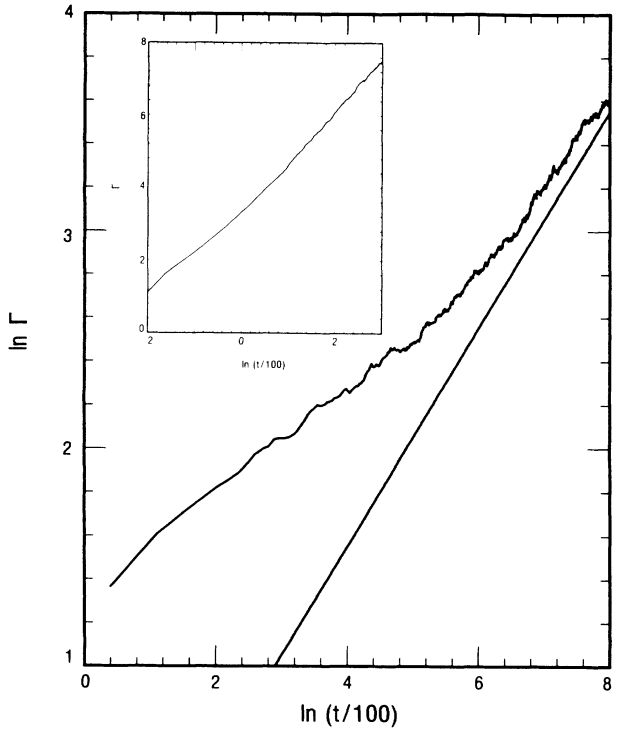

FIG. 2. The logarithm of the coverage vs the logarithm of time for $d=3$ and short-ranged $V(h)$ at $T=2.0J/k$ and with $L=14$; 150 runs of duration 3×10^5 MCS were done to obtain these results. A line of slope $\frac{1}{2}$ is also given in the figure. The inset shows the coverage vs $\ln t$ at short times for $L=14$ and $N=240$.

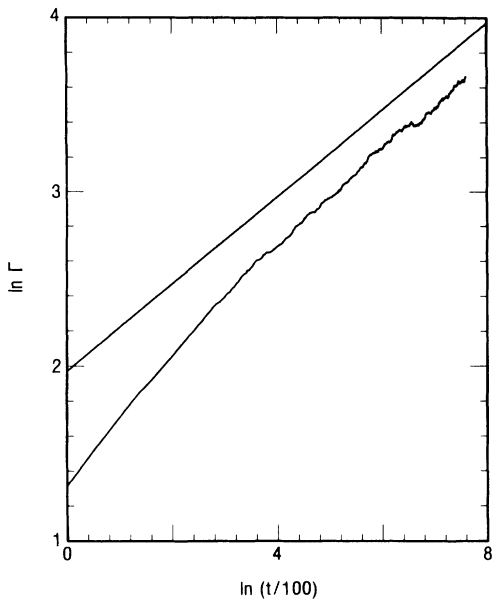

FIG. 3. The logarithm of the coverage is shown vs the logarithm of the time for $d=2$ and a short-ranged $V(h)$ at $T=1.0J/k$ with $L=200$. Some 143 runs of duration 2×10^5 MCS were averaged. A line of slope $\frac{1}{4}$ is included.

large t. A plot of Γ versus $t^{1/2}$ supports this conclusion.

In two dimensions, the short-ranged $V(h)$ again lies in the fluctuation regime. Figure 3 present $\ln\Gamma$ versus $\ln t$ for $L=200$, $T=1.0J/k$, and 2×10^5 MCS, averaged over 143 runs. There is a noticeable curvature in the data for $t<2\times10^4$; at larger times the data approach a line of slope $\frac{1}{4}$. Also, if Γ is plotted against $t^{1/4}$, the result is a line without noticeable curvature for $t>2\times10^4$ as opposed to plots of, e.g., Γ versus $t^{1/3}$ or $t^{1/5}$.

The remaining cases studied in two dimensions, $V(h)\sim h^{-p}$ with $p=1$, 2, and 3, give $\ln\Gamma$ versus $\ln t$ as shown in Fig. 4. The case of $p=1$ is expected to be in the MF regime and to produce $\Gamma\sim t^{1/3}$. The cases of $p=2$ and 3 are expected to be in the FL regime and to produce $\Gamma\sim t^{1/4}$. Comparison of the simulation results with lines of slope $\frac{1}{3}$ and $\frac{1}{4}$ in Fig. 4 shows that these expectations are justified.

For each of the cases just described we have done some runs using values of L different from those given above to check that the results are independent of L and correspond to the large-L limit. Aside from the exceptions already noted [$d=3$ and either $V(h)=0$ or $V(h)\sim h^{-3}$], they are indeed independent of L. As an example presenting the crossover behavior we show Fig. 5 which is a plot of $\ln\Gamma$ versus $\ln t$ for $d=2$, $p=3$, and L of only 30. Lines of slope $\frac{1}{4}$ and $\frac{1}{2}$ are included to guide the eye.

We turn now to consideration of the profiles of the growing films. Figure 6 shows a set of profiles $n(z,t)$ as functions of z for several values of the time for a film growing in the MF regime: $d=2$, $p=1$, $T=0.8J/k$,

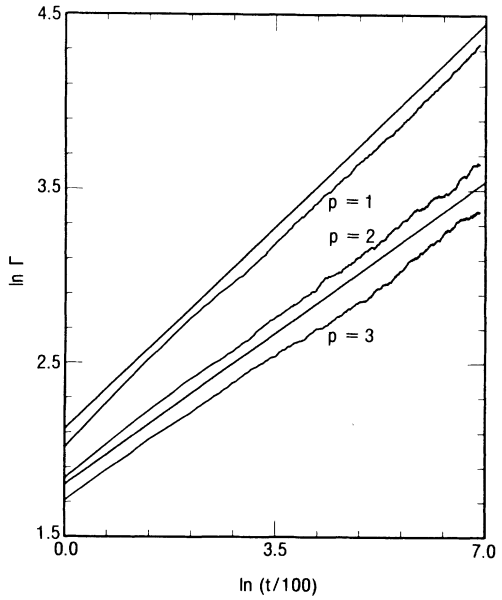

FIG. 4. The logarithm of the coverage is shown vs the logarithm of the time for $d=2$ and an algebraic potential with $p=1$ ($N=60$), 2 ($N=100$), and 3 ($N=120$), for $T=0.5J/k$ and $L=200$. Runs of 10^5 MCS each were employed. Lines of slope $\frac{1}{3}$ and $\frac{1}{4}$ are also shown.

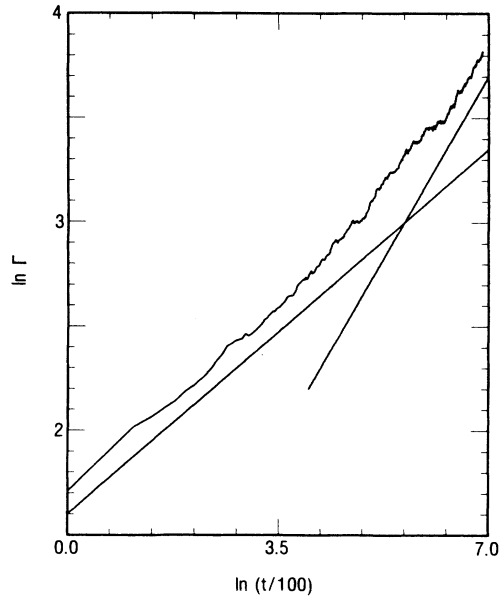

FIG. 5. The logarithm of the coverage vs the logarithm of the time for $d=2$, $T=0.5J/k$, and an algebraic potential with $p=3$. The size of the system was $L=30$, so that the crossover to the small-L regime may be seen; $N=240$. Lines of slope $\frac{1}{4}$ and $\frac{1}{2}$ are also shown.

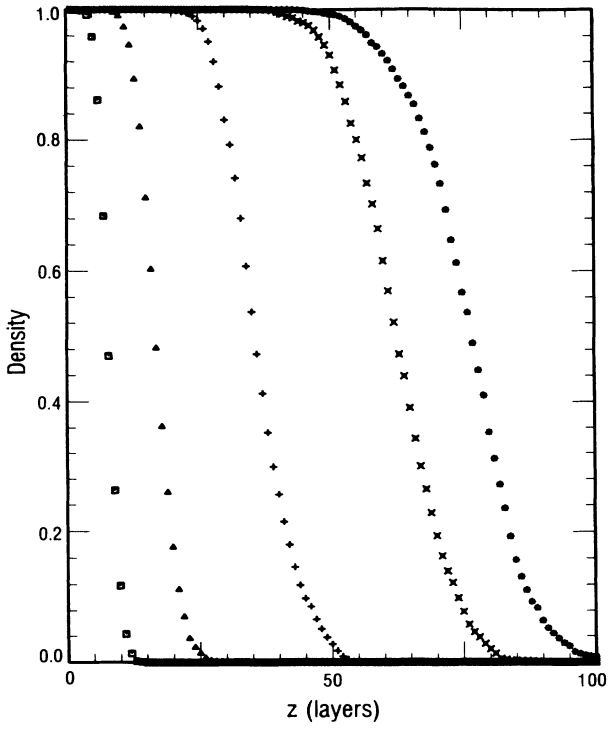

FIG. 6. Profiles $n(z,t)$ as functions of z for times 1 (□), 10 (▲), 100 (+), 500 (×), and 1000 (*) in units of 100 MCS. These are in the MF regime with $d=2$, $p=1$, $T=0.8J/k$, $L=400$, and $N=10$.

and $L=400$. Figure 7 shows the same for a case in the FL regime: $d=2$, $p=2$, $T=0.8J/k$, and $L=400$. The profiles are shown at $t=1$, 10, 100, 500, and 1000 in units of 100 MCS. In both cases the profile broadens as the film grows. In the case of the films in the FL regime, the width of the profile appears to scale as $\Gamma(t)$ itself; that is, if we let the width of the profile be defined as the difference between the values of z where $n=0.10$ and $n=0.90$, this distance appears from our simulations to grow roughly as $t^{1/4}$ reflecting the fact that the film thickness fluctuates at any time by amounts of the order of $\Gamma(t)$. In the mean-field regime our results are less clear. For the case shown in Fig. 6, the width of the profile does appear to increase steadily with time but less slowly than $\Gamma(t)$ which varies as $t^{1/3}$. We have examined also the case of $d=3$ and $p=2$ and again have found that the width of the profile grows less slowly than $\Gamma(t)$. To get a more clear picture of what is in fact happening we would need more runs to provide better statistics.

As for the intrinsic width of the interface defined by Eq. (5), it too increases initially with time but then saturates because of finite-size effects. There is essentially no difference between the behaviors we find for $w(t)$ in the two cases $d=2$ with $p=1$ and $p=2$ which are, respectively, in the MF and FL regimes. For $N=1000$ and runs of 10^5 MCS we find that $w\sim t^{0.24\pm0.02}$ which probably reflects a growth rate with an exponent of one-fourth. However, for other cases in the MF regime in particular, we appear to find quite different growth rates for w. Further studies are underway.

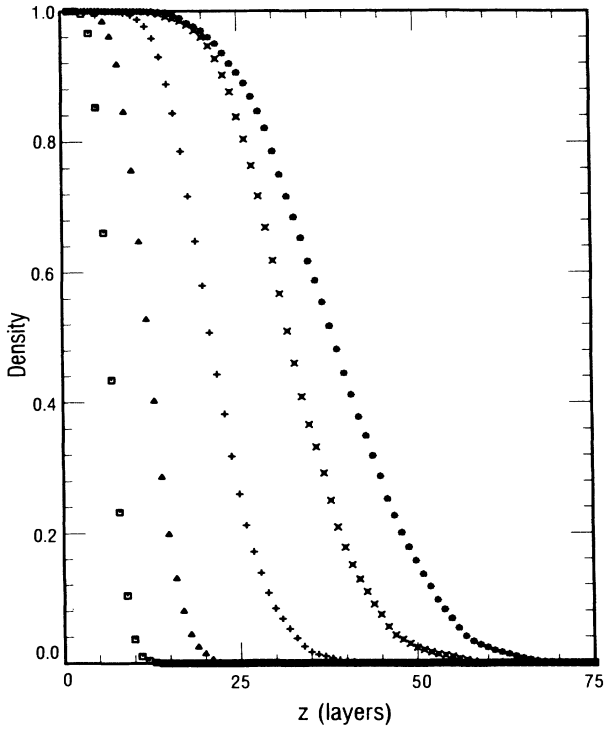

FIG. 7. The same as Fig. 6 but for a case in the FL regime: $d=2$, $p=2$, $T=0.5J/k$, $L=400$, and $N=20$.

IV. SUMMARY AND DISCUSSION

We have used a solid-on-solid model for $d=2$ and 3 to study the growth of wetting films in both the mean-field and fluctuation regimes under conditions of complete wetting at equilibrium. The substrate potentials used are of the forms $V(h)\sim h^{-p}$ with $p=1$, 2, and 3, and $V(h)=0$. The cases $p=2$ and 3 in three dimensions especially are of physical interest as they correspond, respectively, to the van der Waals and retarded van der Waals potentials. The film thickness $\Gamma(t)$ is found to vary at long enough times as $t^{1/\alpha}$, where $\alpha=1/(p+2)$ in the MF regime, and $\alpha=\frac{1}{4}$ in the FL regime in $d=2$. These results are in agreement with the predictions of Lipowsky.[9] For the FL regime in $d=3$, we are unable to employ a large enough system to find unambiguously the claimed $\ln t$ behavior for $L\rightarrow\infty$, but there is certainly some evidence that it is present, as in the simulations of Mon *et al.*,[10] for relatively short times. At larger t there is a crossover to a small-L regime,[10] where $\Gamma\sim t^{1/2}$. The width of the profile of the growing film appears to grow at the same rate as Γ in simulations of one particular case in the FL regime while a somewhat slower growth was observed in simulations involving cases in the MF regime. The intrinsic width of the interface grows until it becomes limited by finite-L effects.

It would be of some interest to pursue the question of the film profile in more detail, looking at correlation functions and the interface width more quantitatively. An additional question worth pursuing is the growth of films given conserved order parameter which would be more appropriate for studies of, e.g., liquid film growth beneath a vapor. Lipowsky and Huse[12] have predicted the behavior of $\Gamma(t)$ in this case, finding in $d=3$ that $\Gamma\sim t^{1/8}$ for $p=2$ and $\Gamma\sim t^{1/10}$ for $p=3$. We are currently looking at the feasibility of simulations that can test these and related predictions.

ACKNOWLEDGMENT

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