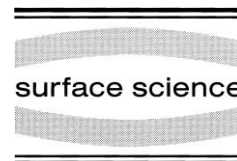




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Growth of amorphous films at low temperatures: the ice model

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Abstract

We present Monte Carlo simulations of the growth of an amorphous ice film on the uniform substrate at low temperatures. The employed 1 + 1 lattice model takes into account anisotropy of interactions between water molecules. In addition, the newly arrived molecules are allowed to relax. The time dependence of the interface width is found to be described by the power law with exponent $\beta=0.28-0.30$, typical for the conventional ballistic deposition models. This finding supports the concept of universality of the growth of amorphous interfaces. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Amorphous surfaces; Models of non-equilibrium phenomena; Monte Carlo simulations; Surface structure, morphology, roughness, and topography; Water

The surface of films growing under conditions far from thermodynamic equilibrium [e.g. during molecular beam epitaxy (MBE)] is often rough [1,2]. Mathematically, this means that the mean-square surface-height difference

$$w^2 = \langle h^2 \rangle - \langle h \rangle^2 \quad (1)$$

increases with time (if the starting condition is a flat surface) as

$$w^2(t) \propto t^{2\beta} \quad (t \ll t_x) \quad (2)$$

where β is the growth exponent. For a system with finite size L , the power law increase of $w(t)$ does not continue indefinitely, but is followed by an

asymptotic regime with

$$w^2(L) \propto L^{2\alpha} \quad (t \gg t_x) \quad (3)$$

where α is the roughness exponent, and t_x is the crossover time ($t_x \propto L^z$, where z is the dynamic exponent). The applicability of the power law expressions (1)–(3) was established by analysing analytically or numerically phenomenological growth equations and various lattice models. The values of the exponents for growth processes are classified by using the universality classes determined by the symmetry properties of the underlying phenomena and by the conservation laws.

The models employed to describe the interface growth [1,2] usually imply that the particle–particle interactions are isotropic. In many cases (e.g. in metal-on-metal MBE), this assumption is reasonable. Often, however, the particle–particle

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interactions are strongly anisotropic. At low temperatures, the anisotropy of interactions may result in the formation of metastable amorphous (or glassy) film structures characterised by abundance of unconnected bonds and/or topological disorder associated with variation in the number of particles forming elementary cells [3,4]. At present, our understanding of the growth of films with such structures is rather limited. In this Letter, we present Monte Carlo (MC) simulations of the formation of an amorphous film disordered due to broken anisotropic bonds. Specifically, our attention is focused on the growth of an ice film during deposition of water molecules on the uniform (e.g. single-crystal metal) surface at low temperatures. This problem is of interest from the point of view of general theory of the interface growth. In addition, it may be related to such interdisciplinary fields of natural sciences as chemistry of heterogeneous atmospheric processes, interstellar and cometary astrophysics, and cryobiology [5,6]. In the context of surface science, the understanding of the growth of ice films might be useful for interpretation of the kinetics of water desorption from or photo- and electron-stimulated processes on the surface or inside of such films (see, respectively, Refs. [6–8], Ref. [5], and Refs. [9,10]).

In nature, water exists in the amorphous ice state at $T \leq 140$ K [11,12]. There are many different forms of amorphous ice with structures and densities dependent on the formation conditions [12]. In general, one should distinguish between the high- and low-density forms of ice. The former are produced e.g. by pressurising a crystalline hexagonal ice. The latter relevant for our simulations are typical for vapor deposition at low temperatures. The fundamental difference in these two categories of ice is that in the latter case the ice structure is highly porous due to a large number of unconnected hydrogen bonds.

To simulate water or ice, one can use the molecular dynamics technique [11,13]. Application of this technique to explore the ice film growth is, however, rather difficult even with current computer facilities. For this reason, we employ in our work the 2D lattice model constructed in analogy with the conventional 2D ice models used earlier

to study entropy of ice at low temperatures [14]. In the framework of our model, the oxygen atoms are located on sites of a square lattice (Fig. 1a). The two hydrogen atoms belonging to a given oxygen atom are oriented along the lines connecting nearest-neighbour (nn) sites so that the angle between their orientations is 90° (the 180° configurations are prohibited). The hydrogen bonds are formed in the cases when a hydrogen atom is located between a pair of nn oxygen atoms. The configurations with two hydrogen atoms between a pair of nn oxygen atoms are not allowed. The water molecules situated in the sites of the bottom row are considered to interact with the substrate also via the formation of hydrogen bonds.

To describe the interface growth, we complement the model introduced above by the kinetic rules corresponding to low temperatures. In particular, the film is considered to be frozen. A water molecule is released from a randomly chosen position above the surface, located at a distance larger than the maximum height of the interface. The molecule follows a straight vertical trajectory until reaching the first site where it can form at least one hydrogen bond (this step is similar to that used in the conventional ballistic deposition models [1]). To form bonds, the molecule is allowed to rotate. If during the motion along the straight line such a site cannot be reached (this may occur due to the ice rule constraints provided that the heights of two columns which are nn to the straight line are equal), the molecule steps down as long as possible and then jumps at random to the left or right in one of the nn sites where it can be bound. After arrival, the molecule forms the maximum possible number of hydrogen bonds with already adsorbed molecules. If there are two configurations corresponding to the minimum energy, one of them is chosen at random. To mimic accommodation of the excess kinetic energy of newly arrived molecules, they are allowed to make N_d attempts of jumps to nn sites. The directions of jumps are chosen at random. A jump trial is considered to be successful provided that (i) it does not violate the ice rule constraints and (ii) the number of hydrogen bonds in the final state chosen among the arrangements with minimum energy is not lower than in the initial state.

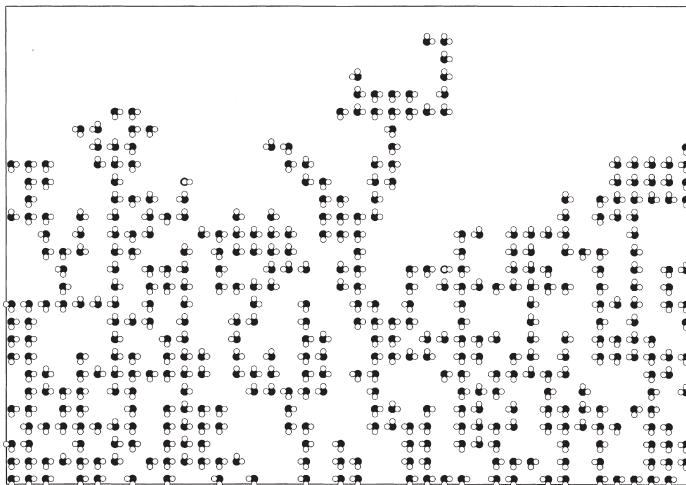
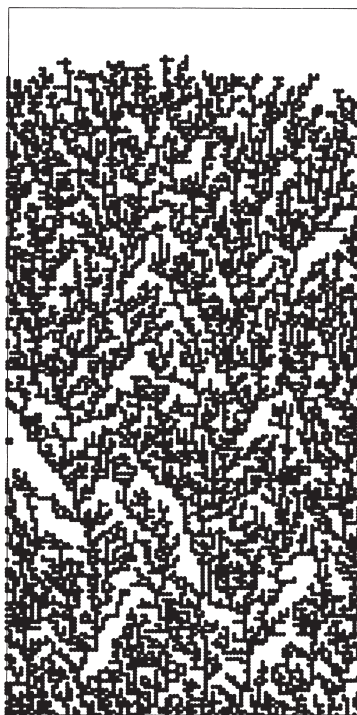
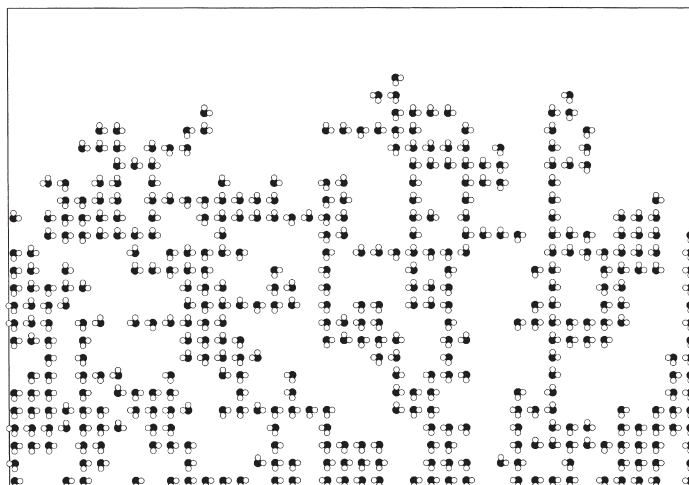
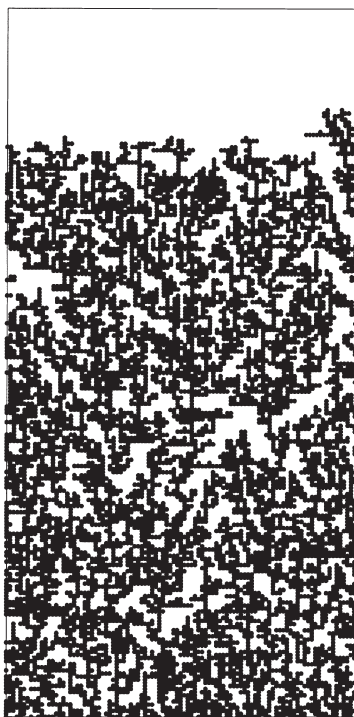
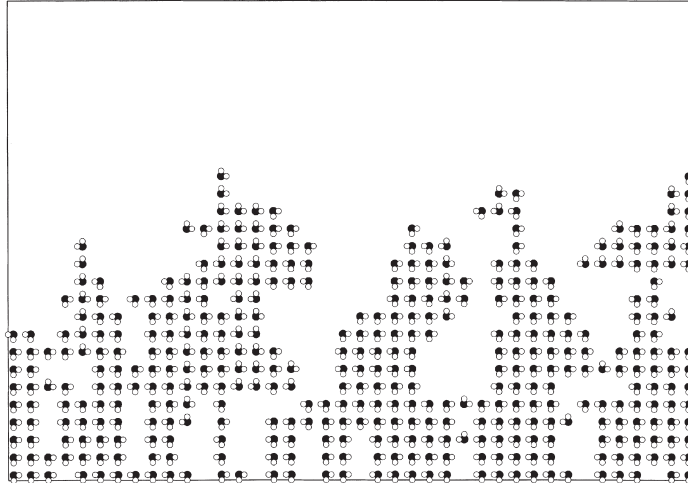
(a) 10 Layers with $N_d=0$ (b) 100 Layers with $N_d=0$ 

Fig. 1. Typical structures of a 2D amorphous ice film formed after deposition of 10 (a) and 100 (b) monolayers of water molecules with $N_d=0$. Oxygen and hydrogen atoms are indicated by filled and open circles, respectively. Hydrogen atoms are shown only on panel (a).

(a) 10 Layers with $N_d=3$ (b) 100 Layers with $N_d=3$ Fig. 2. As Fig. 1 for $N_d=3$.

(a) 10 Layers with $N_d=10$



(b) 100 Layers with $N_d=10$

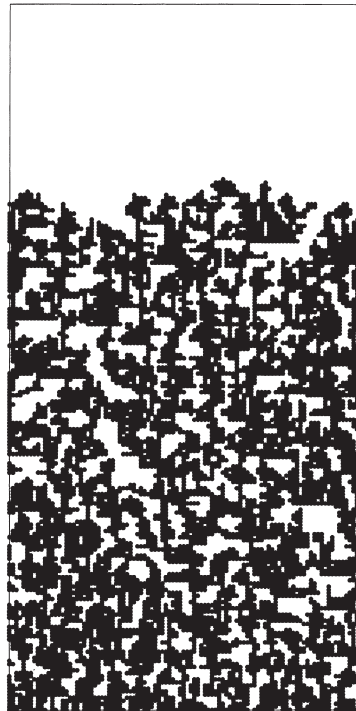


Fig. 3. As Fig. 1 for $N_d=10$.

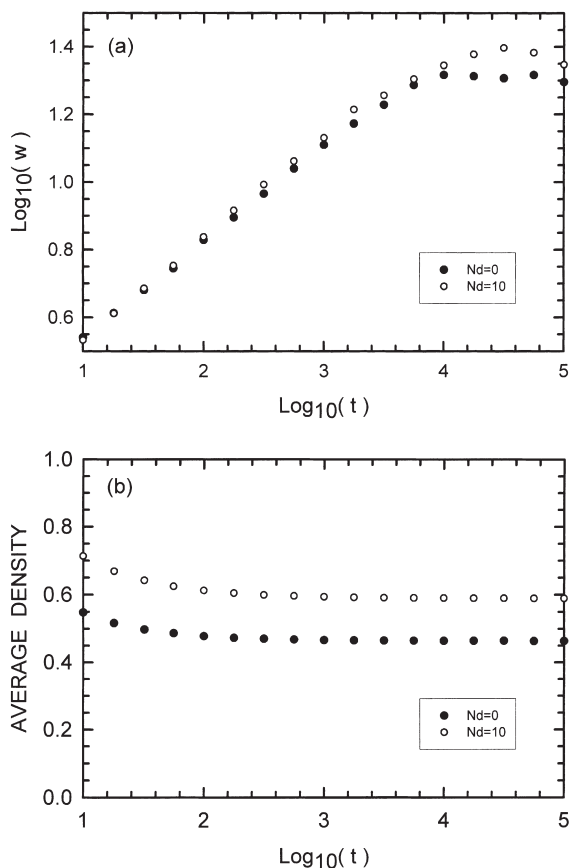


Fig. 4. (a) Mean-square surface-height difference as a function of time (t is calculated in MCS) for the film growth with $N_d=0$ and 10. Each curve is an average of the kinetics obtained in 60 MC runs on the lattice with $L=2000$. The size of symbols shows the statistical error bar at $t \approx 10^4$ MCS. The accuracy of calculations for times shorter and longer than 10^4 MCS is respectively better and slightly worse (in fact, the accuracy is seen from the scattering of the data points). (b) Average density of the film, $\langle \rho \rangle = E/\langle h \rangle$ (E is the exposition in monolayers), during the growth.

Employing the algorithm described above, we have simulated the film growth on the lattice with $L=2000$ and periodic boundary conditions in the lateral direction. The duration of runs was 10^5 MC steps (1 MCS corresponds to deposition of L molecules). The results obtained are shown in Figs. 1–4. In particular, Figs. 1–3 exhibit typical film structures for $N_d=0, 3$, and 10. With increasing N_d , the density of the film is seen to increase slightly and the ice crystallites become larger. The

dependence of the interface width on time (Fig. 4a) is first described by the power law Eq. (2) and then saturates. From the slope of the kinetic curve for $N_d=0$ at $t \leq 10^3$ MCS, we have found that $\beta = 0.28 \pm 0.02$. With increasing N_d , the growth exponent seems to increase but only a little. In particular, $\beta = 0.30 \pm 0.02$ for $N_d=10$.

In summary, our results are in favour of the universality of the growth of amorphous interfaces at low temperatures, because the growth exponents obtained are close to those, $\beta = 0.30$ – 0.33 , reported earlier for conventional ballistic deposition models (see section 8 in Ref. [1]). In all these cases, the non-conservative dynamics (the term ‘non-conservative’ is here related to the formation of holes) are combined with non-conservative noise, and accordingly the lattice models of this type are believed to be associated with the continuum non-linear Kardar–Parizi–Zhang (KPZ) equation (for the 1+1 and 2+1 growth, this equation is known [1,2] to predict respectively $\beta = 1/3$ and 0.20–0.25). With increasing temperature, surface diffusion may modify the KPZ exponents [1,2]. As long as surface diffusion is negligible, amorphous interfaces (e.g. amorphous ice) are expected to be candidates for experimental checks of the applicability of the KPZ theory.

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References

- [1] A.-L. Barabasi, H.E. Stanley, Fractal Concepts in Surface Growth, Cambridge University Press, Cambridge, 1995.
- [2] A. Pimpinelli, J. Villain, Physics of Crystal Growth, Cambridge University Press, Cambridge, 1998.
- [3] S.R. Elliott, in: C.R.A. Catlow (Ed.), Defects and Disorder in Crystalline and Amorphous Solids, Kluwer, Dordrecht, 1994, p. 73.
- [4] H. Sillescu, J. Non-Cryst. Solids 243 (1999) 81.
- [5] D. Chakarov, B. Kasemo, Phys. Rev. Lett. 81 (1998) 5181.
- [6] S. Smith, D.B. Kay, Surf. Rev. Lett. 4 (1997) 781.

- [7] P. Löfgren, P. Ahlström, D.V. Chakarov, J. Lausmaa, B. Kasemo, *Surf. Sci.* 367 (1996) L19.
- [8] F.E. Livingston, J.A. Smith, S.M. George, *Surf. Sci.* 423 (1999) 145.
- [9] M.T. Sieger, T.M. Orlando, *Surf. Sci.* 390 (1997) 92.
- [10] R. Azria, Y. Le Coat, M. Lachgar, M. Tronc, L. Parenteau, L. Sanche, *Surf. Sci.* 436 (1999) L671.
- [11] H.E. Stanley, *Mater. Res. Commun. Bull.* 24 (1999) 22.
- [12] A.J. Kolesnikov, J. Li, S.F. Parker, R.S. Eccleston, C.-K. Loong, *Phys. Rev. B* 59 (1999) 3569.
- [13] E. Stoöckelmann, R. Hentschke, *Langmuir* 15 (1999) 5141.
- [14] R.J. Baxter, *Exactly Solved Models in Statistical Mechanics*, Academic Press, London, 1982.