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# Stochastic ripening of one-dimensional nanostructures

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Ostwald ripening, in which large clusters grow at the expense of smaller ones, is driven by differences in the chemical potentials of these clusters. We demonstrate that ripening can also occur *without* chemical potential differences between small and large particles, by observing the exchange of single atoms between linear chains of Ir atoms; on a $W(110)$ surface these dissociate at a rate independent of length. Ripening takes place because of the stochastic nature of individual atomic events, and is characterized by large fluctuations in the number of exchanges for a chain to disappear. This mechanism should be generally applicable in the ripening of one-dimensional chains, formed on metals as well as semiconductors, and for which the dissociation energy is insensitive to length.

Ostwald ripening is a very general process, identified in solid and liquid solutions, as well as in crystalline films produced by deposition at low temperatures. In this process small clusters dissociate preferentially and lose atoms, which then incorporate into larger entities,[1–7] eventually increasing the mean particle size. The driving force for this transfer is traditionally ascribed to the higher chemical potential of atoms in small as compared to large clusters; this produces a concentration gradient along which atoms flow to the latter. Here we point out, however, that the preferential growth of large clusters is possible even in the absence of *any* differences in the chemical potential, in what we will refer to as stochastic ripening. Such ripening can occur, under the right circumstances, entirely as a result of the random exchange of individual atoms with equal probability between small and large clusters, and should prove generally important for one-dimensional nanostructures, which recently have become of interest on surfaces.[8]

Stochastic ripening has been demonstrated in direct observations of one-dimensional atomic chains of Ir atoms[9] oriented along the $\langle 111 \rangle$ direction on the (110) plane of tungsten, a bcc metal. In Fig. 1(a), two chains, made up of six and eight Ir atoms, respectively, have been assembled on $W(110)$ by depositing roughly a dozen atoms on the surface, and then warming at 430 K to nucleate and grow chains. Once the chains are formed, the surface is heated at 465 K for 3 to 5 seconds, quenched to $\leqslant$30 K and imaged in a field ion microscope (FIM) at 10–15 kV using helium.[10] Each such cycle provides a snapshot of the surface during ripening. The redistribution of atoms between the two chains on repeated heating is apparent in Fig. 1. Only a single long chain is left in the last shot, (g). In this ripening sequence, it is the chain on the left, initially the smaller of the two, that eventually survives, contrary to what is expected in the usual Ostwald ripening.

The evolution of the two chains as time proceeds is shown in more detail in Fig. 2: it seems that the length of the chains oscillates randomly, without regard to the length, until the penultimate snapshot (f). That atom dissociation is indeed independent of length has been established separately in experiments on single chains, in which we have measured the characteristic time for atom detachment. This is just the mean time for one Ir atom to dissociate from the end, to attach itself at the other end of the chain or, as a much less likely possibility, to escape the (110) terrace. As is evident in Fig. 3, the detachment time at 465 K is essentially constant and independent of chain length at an average value of $66.3 \pm 4.9$ sec provided the number of atoms in the chain is five or more. From this size up, the chemical potential is independent of chain length. This is consistent with previous measurements of interaction energies for iridium atoms on $W(110)$: interactions between two adatoms were found to extend over a distance of $\sim$4 nearest-neighbor spacings.[11,12] As the number of atoms in a chain drops to 4 or less, the energy to dissociate an atom from the chain should decrease, and that is indeed confirmed by the detachment data in Fig. 3. For a tetramer, the detachment time at 465 K decreases to $34.2 \pm 7.7$ sec; for trimers, it comes close to zero. The critical

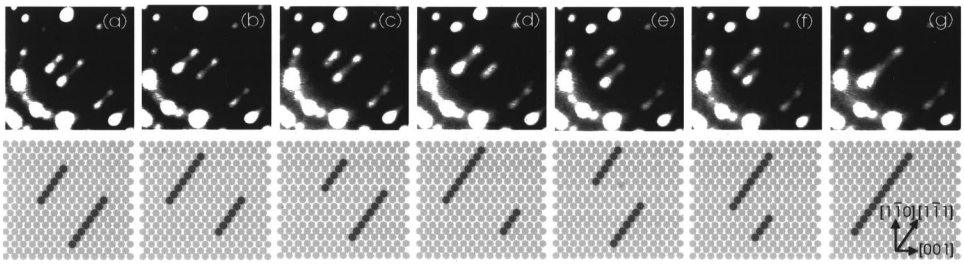


FIG. 1. Ripening of one-dimensional Ir clusters on the $W(110)$ surface, revealed in atomic detail by FIM images at the top, and schematics at the bottom. In (a), two parallel chains have been created by thermal deposition of Ir atoms, followed by nucleation and growth at 430 K. Ripening proceeds at 465 K, in the absence of any applied fields. Evolution of chains was monitored every 5 sec by imaging after cooling the surface to $\leqslant$30 K. (a)–(g) are FIM images at the times indicated in Fig. 2.

 

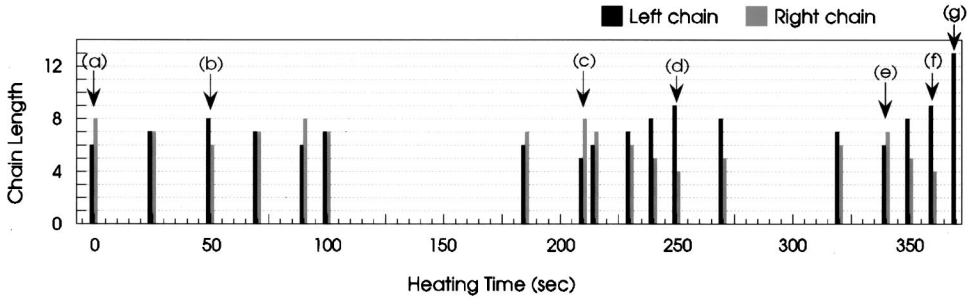


FIG. 2. Evolution of chain lengths with heating time at 465 K. The time each image in Fig. 1 was taken is given by (a)–(g). The length of each chain oscillates as an atom is exchanged between the two chains, but at 185 sec one atom escaped the (110) terrace, and two exchanges occur in the interval from 345 to 350 sec. In the last step of ripening, from (f) to (g), all atoms from the tetramer are incorporated into the larger chain.

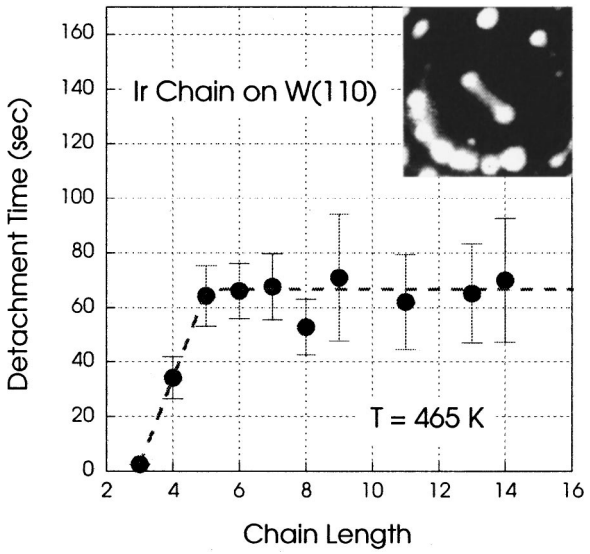


FIG. 3. Time for atom detachment from a single Ir chain at $T = 465\,\mathrm{K}$, as affected by the number of atoms in the chain. Insert: image of a single Ir chain, assembled on $W(110)$ by deposition from a thermal source, followed by nucleation and growth at 430 K. Note that, as expected, the characteristic time for a single chain is longer than for a pair of chains, in Fig. 2.

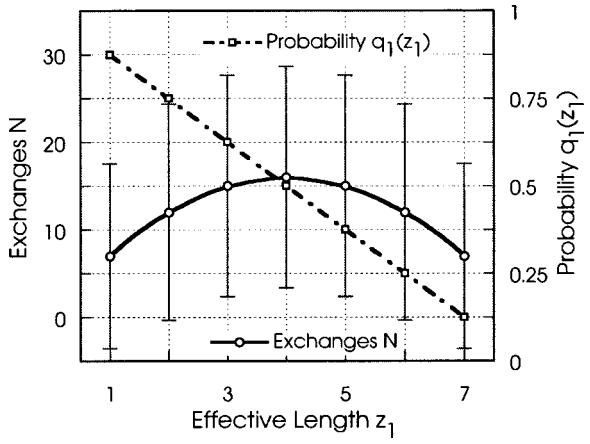


FIG. 4. Dependence of $N$, the mean number of exchanges needed for disappearance of a chain, and of $q_1$, the probability that chain 1 will disappear, upon the effective starting length $z_1$ of chain 1. $z_1$ is the actual chain length corrected for the critical length at which chains disappear immediately. The rms fluctuations $\sigma$ in $N$, shown as error bars, are comparable in magnitude to the number of exchanges $N$. $z_1 + z_2 = 8$ throughout.

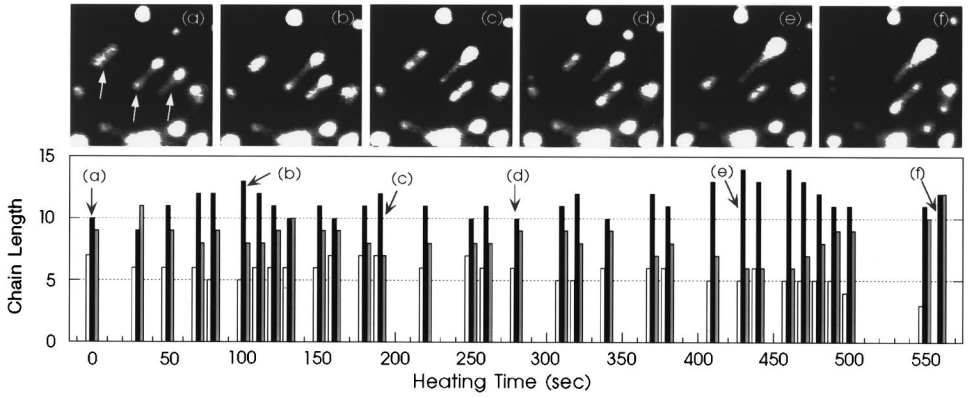


FIG. 5. Evolution of three Ir chains on $W(110)$ by exchange of atoms. In (a), chains made up of 7, 10, and 9 Ir atoms, indicated by arrows, have been formed, and are then monitored after heating at $T = 465\,\mathrm{K}$ for 10 sec; atoms exchange between the chains, causing oscillations in the lengths of the chains. After 550 sec, the chain on the left, initially the shortest, has been reduced to three atoms, and disappears on heating for 10 sec leaving behind two chains of equal length. Field ion images at selected stages at the top, details of the variation in lengths of the Ir chains on the bottom. Once the chain at the left has evaporated, after 560 sec, the evolution of the remaining two chains takes place as in Fig. 2.

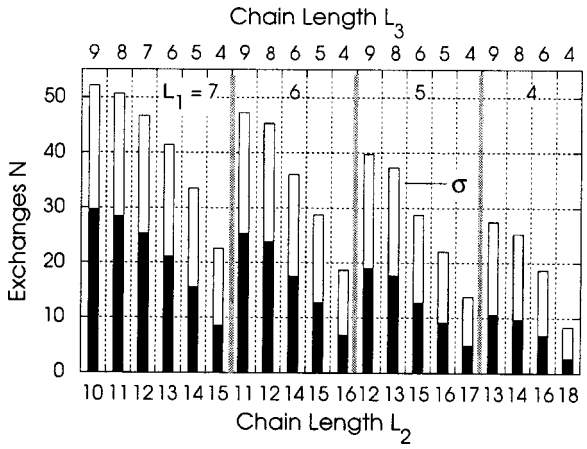


FIG. 6. Mean number of atom exchanges $N$ required for the disappearance of one chain (black bars), and also the rms fluctuations $\sigma$ in $N$ (white bars), are shown for different starting lengths $L_1$, $L_2$, and $L_3$ of three linear chains made up of a total of 26 atoms. Results obtained by Monte Carlo simulations, assuming random redistribution of atoms and a critical length of 3.

length for these chains is three: on heating for five sec a trimer will almost always disintegrate. This accounts for the last step of the ripening sequence, in which all the atoms in the tetramer are lost to the chain of nine atoms at the left. In going from (f) to (g) in Fig. 2, the tetramer at the right presumably lost one atom, and the remaining trimer then disintegrated immediately.

We have also measured the likelihood of single atom loss from the shorter of a pair of Ir chains on $W(110)$. Based on 72 observations, encompassing eight separate ripening sequences at 465 K, we find the probability of atom transfer from shorter to longer chains to be $0.54 \pm 0.06$ for chains with five or more atoms, in good agreement with the value of 0.5 expected for random exchanges independent of chain length.

For two chains in which atom exchange occurs randomly between the chain ends, at a rate independent of the chain length, the likelihood $q_1$ that chain 1 will disappear as atoms are lost and that chain 2 grows is found, by analogy with the classical problem of the gambler's ruin,[13] as

$$q_1 = 1 - z_1/(z_1 + z_2); \tag{1}$$

here $z_1$ and $z_2$ give the number of atoms above the critical length in the two chains. If chain 1 is shorter than chain 2, then the probability $q_1$ that the smaller chain will disappear is greater than 1/2. How long should this process take? The mean number $N$ of atom exchanges until one of the chains disappears is just the product of the two chain lengths,

$$N = z_1 z_2 . \tag{2}$$

The number of exchange events observed in eight experiments for the disappearance of one of the chains is in good agreement (within the expected standard deviation) with the predictions of Eq. (2), provided allowance is made for the rapid loss of atoms from chains with less than four atoms. For example, in Fig. 2, 18 exchanges take place before the chain on the right disappears, compared to 15 predicted from Eq. (2). Overall, in the ripening sequences studied, the ratio of exchanges observed compared to the number expected is $0.9 \pm 0.3$. From our measurements it is clear that the ripening of Ir chains on $W(110)$ is nicely described by a stochastic model. We see here a surprising mechanism for ripening: stochastic ripening, brought about entirely by random exchange of atoms between clusters without any bias favoring larger clusters.

One consequence of the entirely random nature of the dissociation events is that large fluctuations around the average number of exchanges $N$ are expected, with the rms value (or standard deviation) given by[14]

$$\sigma = \{N[(z_1 + z_2)^2 - 2(N+1)]/3\}^{1/2}. \tag{3}$$

For the ripening sequence in Figs. 1 and 2, the standard deviation in the number of events $N$ before one of the chains disappears is expected to be $\pm 12.6$, that is of the same magnitude as the number of events itself. The rms fluctuations are comparable to the mean value of $N$, regardless of the relative length of the two chains at the start, as is shown in Fig. 4. Even for very large chains, $\sigma$ still amounts to $\sim \sqrt{2/3}\, N$ provided they are of roughly equal size.

This unusual process for forming larger clusters is by no means limited to just two chains. A sequence in which iridium chains of 7, 10, and 9 atoms, respectively were assembled on a $W(110)$ surface and then gradually transformed into two by heating at $T = 465$ K is illustrated in Fig. 5. The shortest chain, on the left, does oscillate in length but in this instance never grows beyond its initial size, and finally loses out to the two larger chains. Once the shortest chain disappears the further evolution of the two remaining chains proceeds as shown above. The mean number of atom exchanges $N$ that must take place for one chain to vanish, obtained from kinetic Monte Carlo simulations, is plotted in Fig. 6, for chains of different lengths $L$ built up from a total of 26 atoms.[15] The number of exchanges observed in Fig. 5, namely 35, is in good agreement with the predicted value of 30. However, note again the large scatter around the mean value of $N$. Just as for two chains, in Fig. 4, the number of events $N$ required to eliminate one of the three chains is a maximum when the chains start out at much the same lengths. This maximum value is close to that for only two chains, so that the overall time for the growth of one big cluster starting from three chains will be roughly twice as long as when starting from two chains. Nothing startling should occur as the number of chains increases further, except that coalescence of several chains may intervene.

Critical for the occurrence of the stochastic ripening demonstrated here is the absence of any significant dependence of the rate of atom transfer upon cluster size. In one-dimensional chains the atomic environment around the ends does not change beyond a critical length, provided long-range effects are unimportant. Stochastic ripening should therefore be significant in a variety of systems for which one-dimensional chains have been seen. Bassett[9] first reported the formation of chains for Ni, Pd, Pt, and Ir on the $W(110)$ surface. Linear chains have also been observed for Re on $W(211)$,[16] Pd on Ta(110),[17] Cu on Pd(110),[18] Rh on $W(110)$,[19] as well as Pt on Pt(110)-$(1\times2)$.[20] On Si(100), Si deposited at temperatures around 500 K and small coverages has been observed in long dimer chains,[21,22] but various metals also form long chains on Si(100): Al,[23] Sn,[24] Pb,[25] In,[26]

and Ga.[26] On all such surfaces, stochastic ripening can be expected to contribute to the growth of larger structures as long as dissociation of chains and also atom transport occurs at temperatures lower than does reorganization into two-dimensional structures.

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