

Monte Carlo simulations of icosahedral quasicrystal growth and melting

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Three-dimensional Monte Carlo simulations for atomic growth and melting of icosahedral quasicrystals are presented. It is supposed that the atoms can be locally ordered both icosahedrally and dodecahedrally, and the preferred ordering arises during the growth according to statistical and energetical criteria. All the waiting positions (where an atom could be in principle added) are generated on the cluster surface at every stage of the growth. The binding energies of all atoms and all waiting positions are computed with an oscillating Friedel potential. Then an object, chosen at random from the joined list of surface atoms and waiting positions, is treated according to the Metropolis criterion. The suggested growth process is completely local. It is found that the speed and sign of the process and the resulting structures depend strongly on the growth parameters. Most frequently, the main structural motif of grown clusters is the dodecahedral local ordering (DLO) whereas the icosahedral local ordering (ILO) is usually rare. However, the latter becomes dominant for rather exotic interatomic potentials or for high growth rates. The phenomenon of critical seed size is observed: for those parameters, for which large clusters grow, small enough seeds stop to grow and may even melt. The grown quasicrystals are faceted and their sizes in perpendicular space are rather close to those predicted theoretically and observed experimentally. [S0163-1829(99)11501-7]

I. INTRODUCTION

Statistical methods were applied to quasicrystal growth simulations from the very beginning of quasicrystal science: in one of the first papers, Shechtman and Blech¹ discussed the random packing of icosahedra as a possible model for the just discovered Al₆Mn alloy. Since that time the energetic and entropic approaches are competing for a better description of quasicrystal formation. The idea of Shechtman and Blech was then developed in the so-called icosahedral glass model,²⁻⁴ which considers the growth as a random packing of large identical atomic *clusters* (the Mackay icosahedra or the Bergman triacontahedra) preserving long-range orientational order. The clusters are attached to the growing surface stochastically but with some limitations. The energetic contribution is supposed to be responsible for cluster formation whereas the entropic one works at longer distances.

The *atomic* simulations of growth frequently include the Monte Carlo method for selecting atomic positions where atoms could be added or deleted. However, both in crystals^{5,6} and in two-dimensional quasicrystals,^{7,8} it is usually supposed that the lattice is fixed and the Monte Carlo process determines only the sequence in which those fixed positions are occupied. Olami⁹ showed that if the lattice is not fixed *a priori*, then the growth of slightly defective two-dimensional quasicrystals is possible following some entirely local rules. More recently, Josef and Elser¹⁰ showed that the Monte Carlo growth simulation of a two-dimensional octagonal *tiling* may result in an equilibrium disordered quasicrystal. For the three-dimensional atomic growth of icosahedral quasicrystals, a very effective model was suggested in our recent papers.^{11,12} It produces slightly defective quasicrystals with sizes up to 600 Å. However that model is, strictly speaking,

not local because, at each step, the atom with *the lowest energy* is supposed to be added to the growing quasicrystal. Perhaps the most realistic growth simulations are those ones based on molecular-dynamics studies^{13,14} but they are limited by present computer facilities.

In this paper, a Monte Carlo approach, which is a reasonable combination of energetic and entropic approaches, is applied to three-dimensional icosahedral quasicrystals. In Sec. II the atomic structure of icosahedral quasicrystals and interatomic potentials are discussed. In Sec. III a completely local growth process is suggested. Then, in Sec. IV, the growth rate and the quality of grown quasicrystals are studied. Both growth and melting are simulated as a function of the growth parameters. The problem of initial seeds and the clustering of quasicrystals are discussed in Sec. V. It should be emphasized that we do not consider here electronic effects and vibration entropy effects during growth, melting, and clustering. These effects are, of course, important¹⁵ but in this paper we prefer to focus on effects typical of quasicrystals.

II. LOCAL ATOMIC STRUCTURE AND INTERATOMIC POTENTIAL

The atomic structure of quasicrystals is not yet determined well enough, therefore it is better to leave it as free as possible so that the details of the structure would result from the growth process. Only typical *local* atomic arrangements are fixed in our model; they do not fix the global structure even though they do restrict it. They even allow for periodic structures (so-called quasicrystal approximants). This is an important difference with the growth simulation of crystals: the latter usually presupposes a fixed global atomic lattice.

In our simulations, two types of local atomic arrangements (or ideal local configurations¹⁶) are allowed in accordance with the idealized structure of the approximants¹⁷ and with the best available experimental data on quasicrystal structure.^{18,19}

(1) Icosahedral local ordering (ILO), where the nearest neighbors are at the vertices of a small icosahedron; the interatomic bonds are directed along the fivefold icosahedral axes and their length is r_5 .

(2) Dodecahedral local ordering (DLO), where the nearest neighbors are at the vertices of a small dodecahedron; the interatomic bonds are directed along threefold icosahedral axes and their length is r_3 .

As a result of ILO and DLO, there are also interatomic bonds directed along the twofold icosahedral axes; their length is r_2 . The three lengths, r_2 , r_3 , r_5 , will be referred to as the first coordination shell [see Fig. 1(a)]. They can be easily related to the quasilattice constant a_r : $r_5 = a_r/\tau$, $r_2 = 2r_5/\sqrt{\tau^2 + 1}$, $r_3 = \sqrt{3}r_2/2$ ($r_3:r_5:r_2 = 0.866:0.951:1$, r_2 is about 3 Å in Al-Mn and Al-Pd-Mn alloys). We will not discuss here what are the atomic radii that favor those two types of local ordering (cf. Ref. 11). Because only ILO and DLO are allowed, there are not that many different interatomic bonds in the next coordination spheres [see Fig. 1(a)].

Finally, any possible atomic position, \mathbf{r} , can be expressed as a sum over six base vectors, $\mathbf{e}_1, \dots, \mathbf{e}_6$:

$$\mathbf{r} = \sum_{j=1}^6 n_j \mathbf{e}_j, \quad (1)$$

where n_j are all integer (for *vertex* positions) or all half-integer (for *body-center* positions) and the vectors \mathbf{e}_j are chosen in the following form:

$$\begin{aligned} \mathbf{e}_1 &= \frac{1}{2} r_2 (\tau, 0, \tau^{-1}); \\ \mathbf{e}_2 &= \frac{1}{2} r_2 (\tau^{-1}, \tau, 0); \\ \mathbf{e}_3 &= \frac{1}{2} r_2 (0, \tau^{-1}, \tau); \\ \mathbf{e}_4 &= \frac{1}{2} r_2 (-\tau, 0, \tau^{-1}); \\ \mathbf{e}_5 &= \frac{1}{2} r_2 (\tau^{-1}, -\tau, 0); \\ \mathbf{e}_6 &= \frac{1}{2} r_2 (0, \tau^{-1}, -\tau); \end{aligned} \quad (2)$$

notice that $|\mathbf{e}_j| = r_3$. These six base vectors are directed along the threefold icosahedral axes; however, we could equivalently choose six base vectors directed along five-fold icosahedral axes. We need from Eq. (1) only to describe the two types of local atomic ordering, DLO and ILO.

A further important step is the computation of the atomic binding energy. Central pair potentials are assumed here for interatomic interactions, so that the energy of each inter-

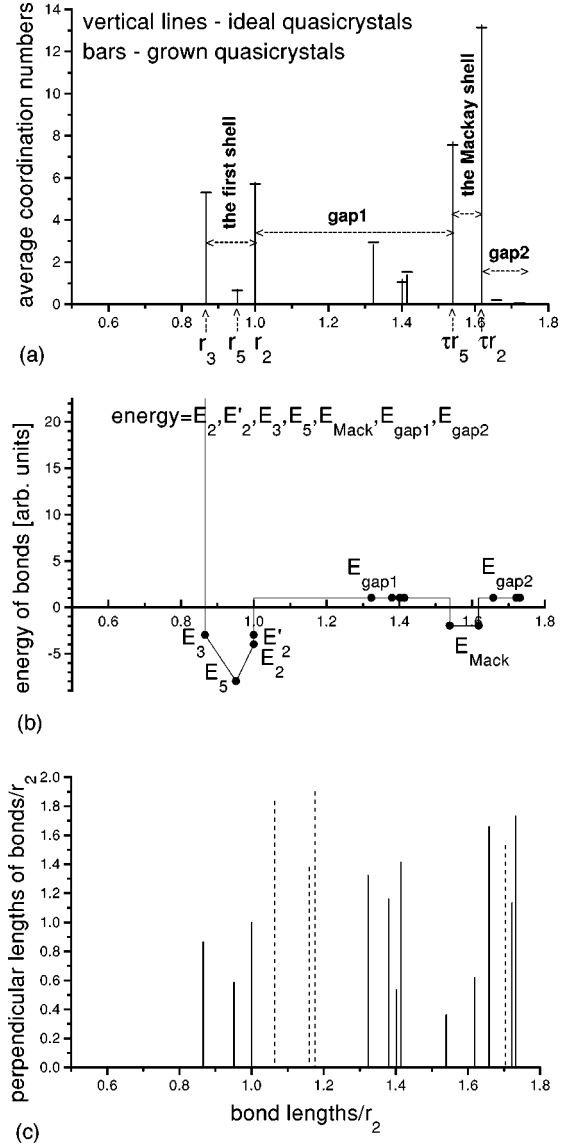


FIG. 1. (a) Typical average coordination numbers, N_c , for different interatomic bonds of different lengths: histogram for ideal quasicrystal, horizontal bars for the Monte Carlo simulations (the difference is extremely small). (b) The interatomic potential with Friedel oscillations used in this paper; the relevant energies, which correspond to the interatomic bonds, are marked with dots; the line is only as a guide for the eye. (c) The perpendicular space lengths of interatomic bonds from (a); those bonds, which exist for the waiting positions but are absent in grown quasicrystals, are shown by dash lines.

atomic bond depends only on the bond length and not on the bond direction. The binding energy of each position is the sum of the bond energies over all the bonds connecting this position with all other atoms. We showed elsewhere^{11,12} that interatomic potentials with suitable Friedel oscillations favor quasiperiodic structures and suppress periodic ones. The oscillating potentials are claimed to be important for the stability of quasicrystals²⁰⁻²⁴ (see especially discussion in Ref. 24). Therefore, here too we use potentials oscillating with the interatomic distance [Fig. 1(b)] and restrict the range of these potentials to $2r_3$ (i.e., about 5 Å). The latter restriction is introduced not only for computational reasons but because of the low conductivity of quasicrystals the oscillations should

be damped at high and normal temperatures (see however²⁵ where a mechanism of enhancement of the Friedel oscillations in quasicrystals is suggested). Only those values of potentials are of real importance which correspond to the possible bond lengths [they are marked by dots in Fig. 1(b)].

The significance of the oscillating potentials just for quasicrystals is demonstrated by Fig. 1(c) in which the lengths of the interatomic bonds in the so-called perpendicular space are plotted. According to Eq. (1), any atomic position, \mathbf{r} , of a DLO/ILO lattice can be lifted into a six-dimensional cubic lattice so that n_1, \dots, n_6 are its six-dimensional coordinates. Then its projection, \mathbf{r}_\perp , onto perpendicular space can be found:

$$\mathbf{r}_\perp = \sum_{j=1}^6 n_j \mathbf{e}_{\perp j}, \quad (3)$$

where the vectors $\mathbf{e}_{\perp j}$ are given by

$$\begin{aligned} \mathbf{e}_{\perp 1} &= \frac{1}{2} r_2(\tau, \tau^{-1}, 0); \\ \mathbf{e}_{\perp 2} &= \frac{1}{2} r_2(0, \tau, \tau^{-1}); \\ \mathbf{e}_{\perp 3} &= \frac{1}{2} r_2(\tau^{-1}, 0, \tau); \\ \mathbf{e}_{\perp 4} &= \frac{1}{2} r_2(\tau, -\tau^{-1}, 0); \\ \mathbf{e}_{\perp 5} &= \frac{1}{2} r_2(0, \tau, -\tau^{-1}); \\ \mathbf{e}_{\perp 6} &= \frac{1}{2} r_2(-\tau^{-1}, 0, \tau). \end{aligned} \quad (4)$$

The perpendicular projections of the interatomic bonds should not be too large in order to avoid very short interatomic distances. It is obvious from Fig. 1(c) that the maxima of the selected potential correspond usually to the bonds with larger perpendicular lengths; hence those bonds will be suppressed or, may be, completely absent.

III. GROWTH PROCESS

The suggested growth process includes the following steps (see afterwards detailed comments about each step).

- (i) The growth starts from an initial seed cluster of atoms.
- (ii) New admissible atomic positions are generated around the quasicrystal at each stage of the growth (they will be referred to as waiting positions) and ‘‘dangling’’ atoms are deleted.
- (iii) The energies of all the atoms and of all the waiting positions are computed with the interatomic potentials discussed above

(iv) An object, chosen at random from the joint list of surface atoms and waiting positions, is treated according to the standard Metropolis criteria: (a) if the energy of the atoms on the surface is larger than its energy in the liquid—the atom is deleted, if it is smaller—the atom may be deleted

with a probability given by the Boltzmann distribution; (b) if the energy of the waiting position on the surface is smaller than its energy in the liquid—the position is occupied by an atom, if it is larger—the position may be occupied with a probability given by the Boltzmann distribution.

(v) If an atom is deleted or added we go to (ii); if not, we repeat (iv).

The following comments should clarify this procedure.

Comment to (i): We use as initial seeds spherical pieces of an ideal face-centered quasicrystal. This ideal quasicrystal has three acceptance domains in perpendicular space:²⁶ a triacontahedron for even nodes (all n_j are integer and $\sum_{j=1}^6 n_j = 2n$), a fivefold-ruffled triacontahedron for odd nodes (all n_j are integer and $\sum_{j=1}^6 n_j = 2n + 1$), and a small triacontahedron for even body centers of the six-dimensional cubic lattice (all n_j are semi-integer and $\sum_{j=1}^6 n_j = 2n$). The seeds should be large enough since small seeds do not grow and may even melt (see Sec. V).

Comment to (ii): ‘‘Admissible’’ means that (a) new positions obey the DLO and/or ILO with respect to the old atoms and (b) each new position has three or more atoms in the first coordination shell (i.e., in direct contact). The latter condition is needed because the interatomic bonds in metals are not directional and the contacts with at least three atoms are needed to fix the position of any atom in space. Hence ‘‘dangling’’ atoms, which have only one or two first-shell neighbors are not permitted and they are deleted immediately.

Comment to (iii): The binding energy of any position, E_{bind} , is computed as a sum of energies of all the bonds connecting this position with atoms of the growing quasicrystal:

$$E_{\text{bind}} = - \sum_{\text{bond}} N_{\text{bond}} E_{\text{bond}}(r_{\text{bond}}), \quad (5)$$

where N_{bond} is the number of bonds with the energy $E_{\text{bond}}(r_{\text{bond}})$; the sign is chosen in such a way that a greater binding energy means a stronger binding of the atom. To speed up the computations, all the bond energies are supposed to be integers. The energy of each bond may be considered as an independent parameter. To minimize the number of the independent parameters, the bonds are divided into groups and the same energy is assigned to the bonds within each group. In this paper, the potential is described by seven parameters [Figs. 1(a) and 1(b)]: E_2 (E'_2) is the energy of the r_2 bonds between two large (small) atoms; E_3 is the energy of the r_3 bonds between large and small atoms; E_5 is the energy of all r_5 bonds; E_{Mack} is the energy of all the τr_5 and τr_2 bonds of the Mackay shell (the outer shell of the Mackay icosahedron); E_{gap1} is the energy of all the bonds which are in the gap between the first shell and the Mackay shell; finally, E_{gap2} is the energy of all the bonds which are in the second gap in coordination numbers just beyond the Mackay shell ($\tau r_2 < r \leq 2r_3$). In addition, we assume that no bond is shorter than r_3 (hard sphere approximation). Previously¹¹ we assumed that $E_2 = E'_2$; in that case the interaction between large and small atoms becomes completely symmetric. The resulting symmetry of the grown quasicrystal is primitive icosahedral. In contrast, if $E_2 \neq E'_2$, the symmetry becomes face-centered icosahedral.¹² This is a minimal scheme to maintain the distinction between large and small atoms. No-

tice that the chosen oscillating potential suppresses automatically those bonds which have larger lengths in perpendicular space [Fig. 1(c)] because in the physical space they correspond to positive values of the potential. This is why the growing quasicrystals are so severely restricted in perpendicular space (see Sec. IV). In fact, the energies of atoms and waiting positions are computed and recomputed during the (ii) step, so that no additional runs are needed for the energy computation.

Comment to (iv): To apply the Metropolis criteria, the difference in energies, ΔE , of atoms on the surface and in the liquid must be found. Obviously, $\Delta E = (E_{\text{bind}} + E_{\text{sf}}) - E_{\text{ff}}$ where E_{sf} is the interaction energy of a surface atom with fluid and E_{ff} is the interaction of a fluid atom with fluid. It is assumed that E_{sf} does not depend on the atom environment and the difference, $\Delta\mu = E_{\text{sf}} - E_{\text{ff}}$, is an independent parameter which governs the growth and melting (adsorption and desorption): atoms with $E_{\text{bind}} > \Delta\mu$ have a tendency to be adsorbed on the surface whereas atoms with $E_{\text{bind}} < \Delta\mu$ have a tendency to be desorbed from the surface into fluid. The Metropolis rule describes both tendencies quantitatively: (i) an atom is attached to the randomly chosen waiting position if $\Delta E \leq 0$ and it is attached with probability $\exp(-\Delta E/kT)$ if $\Delta E > 0$; (ii) a randomly chosen atom is deleted from the surface if $\Delta E > 0$ and it is deleted with probability $\exp(\Delta E/kT)$ if $\Delta E \leq 0$.

As a result, detailed balance is obeyed as we have checked. Atoms with more than eight first-shell neighbors are considered as bulk atoms and the Monte Carlo procedure is not applied to them; thus, in our model, atoms cannot disappear from the bulk.

IV. GROWTH AND MELTING

For this initial study, we fix the energetic parameters of the model as shown in Fig. 1(b). From the experience with our previous pure-energetic model we know that the growth with these parameters produces faceted quasicrystalline grains of rather good quality. In addition, we let the temperature vary in a small interval around the melting point. Thus, the temperature variations (superheating and supercooling) affect only $\Delta\mu$ which is proportional to the temperature, so that $\Delta\mu = \mu_{\text{melt}} + \alpha(T - T_{\text{melt}})$, whereas kT is supposed to be constant and equal to kT_{melt} ; $kT_{\text{melt}} = 3$ in the chosen energy units.

The dynamics of the growth and melting process is shown in Fig. 2 and Fig. 3 for various amount of supercooling ($\Delta\mu < \mu_{\text{melt}}$) and superheating ($\Delta\mu > \mu_{\text{melt}}$). The growth (melting) rate is shown in Fig. 4 (the number of attempts is proportional to the time of growth). We see that for strong supercooling the grains grow proportionally to time, whereas for weak supercooling the growth is not linear: small grains grow slowly. The latter is a natural effect of greater (on the average) surface curvature of smaller grains; where the curvature is strong the binding energy is smaller. Another interesting effect observed at weak supercooling is the stepwise character of the growth (a slowing down of the growth for some typical numbers of atoms). This is a result of the inhomogeneous layered structure of quasicrystals. Indeed, when the growing quasicrystal reaches a layer with lower density and lower cohesive energy, the growth becomes slower. This

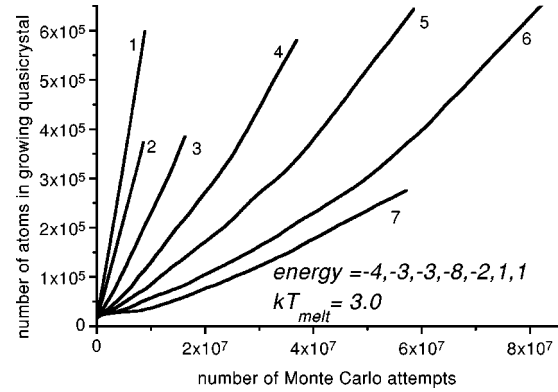


FIG. 2. Number of atoms in growing quasicrystals for different amounts of supercooling ($\Delta\mu < \mu_{\text{melt}}$) as a function of the number of attempts (the latter is proportional to the growth time). The growth starts with an ideal spherical seed of about 15000 atoms. The growth rate is smaller in the beginning because the average binding energy is smaller owing to the surface curvature; this effect is practically absent at stronger supercooling. At the very initial stage (not shown) the seed may be slightly melted because on the spherical surface there are not many enough sites available for growth. $\Delta\mu = 33.0$ (1), 34.0 (2), 35.0 (3), 35.5 (4), 35.8 (5), 36.0 (6), 36.1 (7).

slowing down is more pronounced for melting (Fig. 3) and for small clusters (the latter will be considered in Sec. V). At strong superheating the grains melt proportionally to time, whereas at weaker superheating the melting process is not linear: it can even come to a stop when it reaches a surface with a higher cohesive energy of atoms.

The shape of the grown quasicrystalline grains is usually dodecahedral in the beginning and then becomes more rounded; thus it is not yet clear whether the large grains are

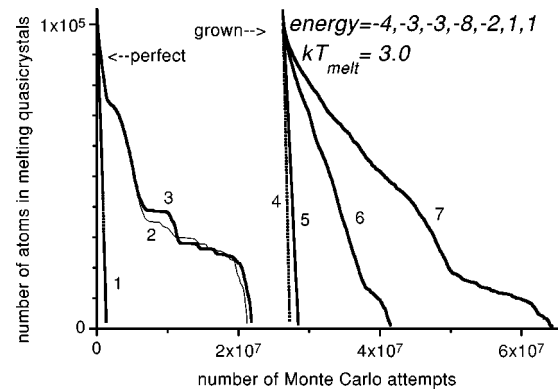


FIG. 3. Number of atoms in melting quasicrystals for different amounts of superheating ($\Delta\mu > \mu_{\text{melt}}$) as a function of the number of attempts (or time). The melting starts either with an ideal spherical grain (1, 2, 3) or with an as-grown ($\Delta\mu = 36.1$) quasicrystal (4, 5, 6, 7), both of about 105000 atoms. $\Delta\mu = 45.0$ (1, 4), 42.0 (2, 3, 5), 40.0 (6), 39.7 (7). Curves 2 and 3 demonstrate different realizations of the Monte Carlo process below 45 000 atoms. The melting is faster at the very beginning because it is difficult to add new atoms on the smooth spherical surface of the initial grain and at the very end because the average binding energy is smaller owing to the large surface curvature. For the melting of the grown quasicrystal, the melting is slower below 15000 atoms (curves 6 and 7) because the initial seed has the ideal structure.

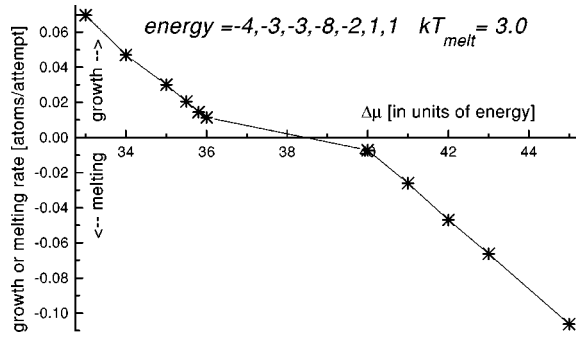


FIG. 4. Growth (melting) rate of quasicrystals as function of $\Delta\mu$. The growth rates are taken from Fig. 2 between 4×10^5 and 5×10^5 atoms, and the melting rates are taken from Fig. 3 between 2×10^4 and 9×10^4 atoms.

faceted. Indeed, to find the growth faceting of macroscopic samples, we should find and compare the growth rate of different facets but this would take a lot of computational time and is beyond the scope of the present work.

The structure of grown quasicrystals is similar to the ideal one: most of the atoms have their nearest neighbors at the vertices of a small dodecahedron (DLO). The amount of atoms with the purely icosahedral local coordination (ILO) is only about 3%. The coordination numbers of the grown and ideal quasicrystals are also very similar [see Fig. 1(a)]. The ILO is in minority in spite of our efforts to enlarge its presence by choosing a stronger icosahedral binding ($E_5 = -8$) in comparison with dodecahedral binding ($E_3 = -3$). Strong icosahedral coordination is observed only in the next coordination sphere. On the average, each atom has about 7.5 neighbors at distance τr_5 (this is just the edge of the Ammann rhombohedra). In average, there are 20.7 atoms in the Mackay shell (distances τr_5 and τr_2), that is one half of the complete Mackay icosahedron. This means that there are many almost complete pseudo-Mackay icosahedra. On the other hand, those minor atoms with icosahedral coordination have almost 20 neighbors at distance τr_3 (i.e., at the vertices of large dodecahedron); this yields a 33-atom cluster²⁶ ($1 + 12 + 20$) which is a part of the Bergman triacontahedron.

The surface of the grown quasicrystals is rather rough. Nevertheless, the topmost atomic layers are similar to the structure met in *flat* atomic layers observed after annealing:²⁷ the surface is covered by small icosahedra, and their shells, together with atoms in between, produce the two topmost layers (or one dense puckered layer) whereas their centers produce the third layer. Such a structure is a result of a rather large ratio E_5/E_3 , so that each icosahedron tends to be completed (in Ref. 27 those icosahedra are supposed not to be complete: the topmost vertices are absent). But of course, because of the growth, some atoms violate this surface structure and this description works better for slow growth, melting and annealing or, even better, for stable clusters (see below).

The ILO becomes more common for stronger supercoolings (i.e., for smaller $\Delta\mu$); for the considered energy, small ILO clusters appear as interstitials if $\Delta\mu = 30.0$ and they become larger and more numerous for $\Delta\mu = 20.0$. It is not clear, however, whether these values of $\Delta\mu$ are physically accessible. Changing the interatomic potentials (for example, increasing E_5/E_3), it is possible to grow quasicrystals with

pure ILO. In these quasicrystals only two types of lattice positions are occupied (say, even vertices and even body centers). However, it is possible to select a deflated cubic lattice with τ times smaller size (in the general case it would be a face-centered icosahedral lattice) where only vertices are occupied (no body centers). Hence, these quasicrystals should have a τ times inflated diffraction pattern. In our simulations these ILO quasicrystals always have rather large and quickly growing sizes in perpendicular space and rather small atomic density. This may be why they have never been observed, to the best of our knowledge. However it is interesting to note that there exists an approximant of these ILO quasicrystals, the well-known Al_{12}W structure, with pure ILO of atoms and having a diffraction pattern τ times inflated in comparison with other Al-transition-metal approximants (usually Al_{12}W is wrongly considered as an approximant of conventional Al-Mn and Al-Mn-Pd quasicrystals).

Figure 3 shows the melting dynamics of ideal and as grown (slightly defective) quasicrystals. The ideal quasicrystal is constructed as described in the comment to (i) above. There is a remarkable difference in the melting rates: for the same $\Delta\mu$ the ideal quasicrystal melts more slowly. It means that even a small amount of phason defects can strongly change the melting rate; this phenomenon may be important for the improvement of quasicrystal quality because, in real slow growth, the alloys crystallize and melt locally many times before final crystallization. Notice again the steplike character of melting which is especially pronounced at weak superheating and in ideal quasicrystals. The melting process does not proceed as reversed growth: in the beginning the surface becomes rough and appears to be covered by small clusters. Then the clusters become larger (containing about 1900 atoms) and more stable: the plateaus on the melting curve (Fig. 3, curves 2 and 3) correspond to situations when the clusters do not melt and the smallest step between two plateaus just reflects the melting of one cluster. For grown (hence imperfect) quasicrystals the melting-induced clustering on the surface is less pronounced. We conclude that the clustering on the surface is quite typical for the melting process but it is not clear yet what is the equilibrium spectrum of the cluster sizes. In order to get quantitative results, detailed simulations of the growth of an isolated surface are needed, at least for twofold, threefold and fivefold surfaces; this work is now in progress.

In order to characterize the quality of the grown quasicrystals (their phason disorder), they are lifted to the six-dimensional cubic lattice and their projections on the perpendicular space are computed in accordance with Eq. (3) (Fig. 5). These projections are three-dimensional clouds of dots, each dot being the projection of one atomic position; in the two-dimensional figure many projections coincide. The number of even and odd lattice points is different, implying that the grown quasicrystal has a face-centered icosahedral lattice. Notice that the clouds are only slightly larger than the atomic surfaces of the ideal quasicrystal and they slowly increase in size throughout the growth. Figure 6 shows the mean-square radius, $\langle r_{\perp}^2 \rangle$, of the clouds as a function of the physical-space distance from the center of the growing quasicrystals. For each distance, we find $\langle r_{\perp}^2 \rangle$ within a spherical shell about $2r_2$ thick. For the sake of simplicity, $\langle r_{\perp}^2 \rangle$ is computed altogether for both types of vertices and both types

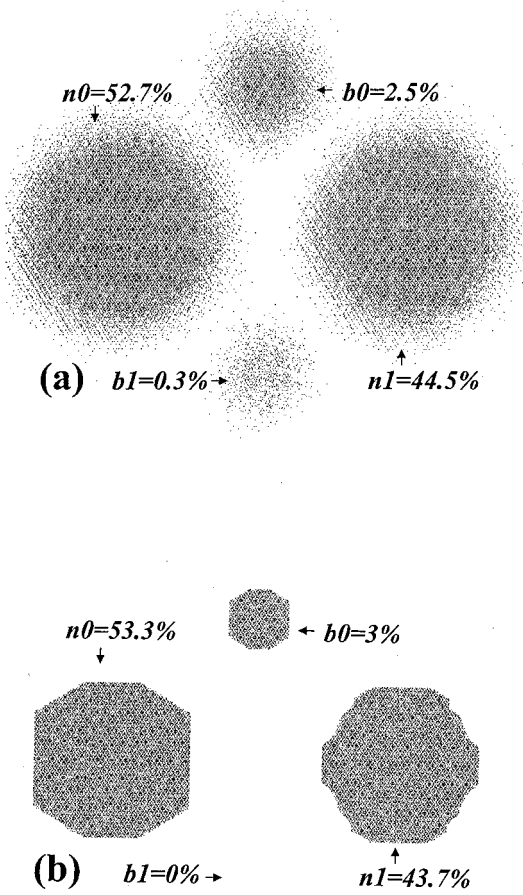


FIG. 5. (a) View along a twofold symmetry axis of a grown cluster (450 000 atoms, $\Delta\mu=35.0$) in perpendicular space. The dots are projections of the even (odd) vertices, $n0$ ($n1$), and the even (odd) body centers, $b0$ ($b1$); they are shifted in the figure plane to show them separately (in reality the centers of gravity of those four projections should coincide). (b) Same view of the ideal face-centered quasicrystal²⁶ (the large triacontahedron for $n0$, the fivefold-ruffled triacontahedron for $n1$, the small triacontahedron for $b0$, and nothing for $b1$). Relative concentrations of different vertices are shown in percentage.

of body centers of the face-centered icosahedral lattice according to the same formula:

$$\langle r_{\perp}^2 \rangle = \frac{1}{N} \sum_{i=1}^N \left(r_{\perp i} - \frac{1}{N} \sum_{j=1}^N r_{\perp j} \right)^2, \quad (6)$$

where N is the total number of atoms in the layer. Of course, the perpendicular sizes increase with increasing number of atoms (hence the phason disorder increases as well). Yet, this increase may be smaller than for our previous approach¹² when the best atom was stuck each time (curve “old” in Fig. 6). It is not clear whether the perpendicular size tends toward some finite value; in our previous simulations we have found that for 10^7 atoms the perpendicular size increases up to 30% above the size of the ideal quasicrystal (the real-space size is about 600 Å, similar to the coherence length of Al-Mn quasicrystals). It should be emphasized that there is no phonon

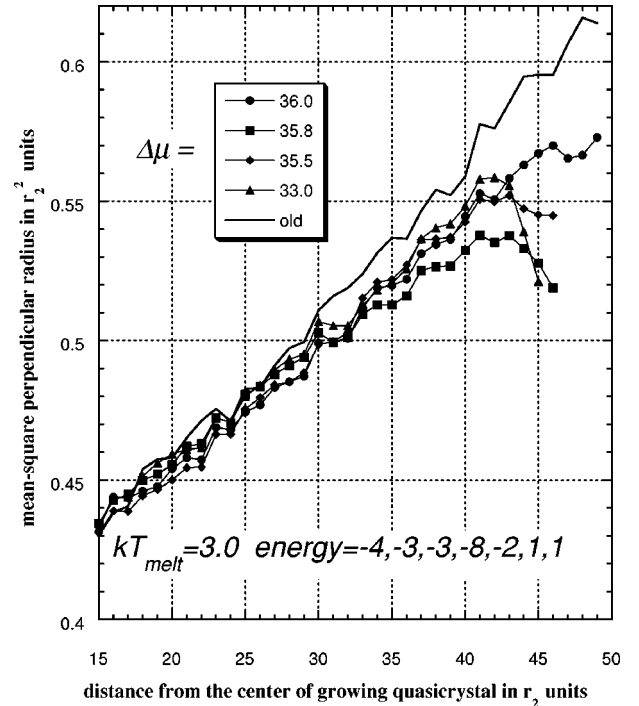


FIG. 6. The mean-square perpendicular-space size, $\langle r_{\perp}^2 \rangle$, of growing quasicrystals for different supercoolings $\Delta\mu$ as a function of the physical-space distance from the center of growing quasicrystals. For the ideal quasicrystal the mean-square size is about 0.4. The curve “old” corresponds to the growth process when the atom with the best energy is added to the quasicrystal. The drop at extremities of the curves occurs because sites on the surface have a smaller mean-square perpendicular size than bulk positions.

disorder in this growth model because the shortest interatomic distances r_3 , r_5 and r_2 are fixed.

V. STABLE CLUSTERS

Here we present a few results concerning the problem of cluster formation during growth and melting; a more detailed presentation will be given elsewhere. An interesting phenomenon is observed if we begin the Monte Carlo process from a small seed and choose μ so that large grains grow slowly (i.e., if μ and the temperature T are only slightly below the melting point). In this case the result depends on the seed size: the seed either grows or melts and approaches one of a set of typical clusters which are very stable and only fluctuate a little around some intrinsic form and size.

Examples are shown in Fig. 7. If there are less than 300 atoms in the initial ideal seeds, the seeds melt. For about 350 atoms, the seed, at random, either melts or grows and then fluctuates around a “stable” cluster which contains about 440 atoms (its shape is approximately dodecahedral). Larger clusters (up to 600 atoms) also approaches to this stable cluster. This cluster is only relatively stable: a large enough fluctuation, which, of course, has a very small probability, can provoke either melting or further growth. The next “stable” cluster contains about 1050 atoms and its shape is approximately icosahedral. After that, the next “stable” cluster of about 4300 atoms the shape is triacontahedral in shape. In this case, the stepwise growth is rather obvious: this means

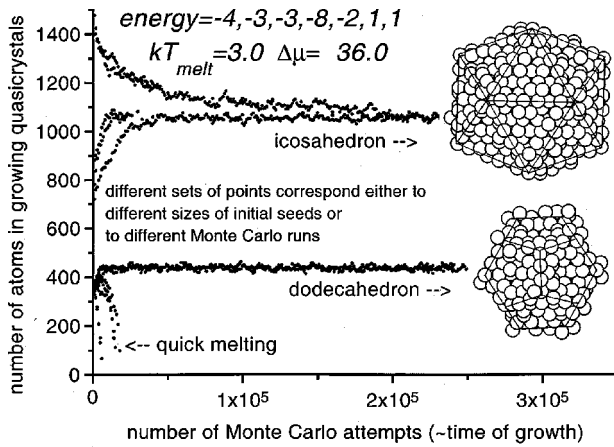


FIG. 7. Formation of stable clusters; different sets of points correspond either to different initial seeds or to different runs of the Monte Carlo process.

that there are several closely spaced minima of the cluster energy.

The bulk structure of the stable clusters is practically equivalent to the structure of ideal quasicrystals; even if there is some growth, the grown part is rather thin and the phason disorder in it is very small. The structure of the grown cluster surface is similar to that of slowly grown or melted quasicrystals: the layers of small icosahedra form something like a crust on the surface and stabilize it against further growth or melting.

Above we used as initial seeds spherical clusters which are cut from an ideal quasicrystal so that they have a body-center position at their center (both in real and in perpendicular space). Thus there is a small icosahedron around the central atom of the seed. When we change the position of the center, the sizes of “stable” clusters may also change. For example, if we take spherical seeds with a pseudo-Mackay icosahedron at the center, they melt completely as long as they contain less than 1100 atoms, whereas in the range between 1300 and 2900 atoms they tend to a “stable” cluster of about 1900 atoms. The latter is just the cluster which arises on the partly melted surfaces.

The dependence of the size of the clusters on the initial seeds is rather natural because (i) the structure of quasicrystals is nonhomogeneous on this scale (about ten interatomic distances) and (ii) with the Monte Carlo method it is difficult to reach absolute equilibrium if the barriers are large enough. This shows us the limitations of the suggested Monte Carlo procedure. But it seems that the physical result is valid in spite of the limitations of the model: the “stable” clusters survive longer than others even if they eventually do melt or start growing. In other words, the solidification (melting) temperature of quasicrystalline clusters should depend on their size (this phenomenon is well known for crystalline clusters as well^{28,29}). Perhaps it is possible to fix (quench) these clusters in real alloys if the growth conditions vary rapidly enough (clusters of comparable sizes, 10^3 to 10^4 atoms, were observed³⁰ in Ca).

VI. DISCUSSION

The preliminary results obtained in this paper show that now we have a reasonable growth model which is worthy of

further studies (the growth of different planes with different potentials, different kT_{melt} , annealing of grown clusters). The proposed Metropolis algorithm is entirely local. Nevertheless, it allows to obtain atomic structures close to those that have been theoretically suggested as well as experimentally determined for actual quasicrystals. In our model there is no need of large ready-made clusters and the clusters arise as a result of growth; but of course, any additional mechanism which favors cluster formation³¹ could improve the quality of the final structure. It is typical of quasicrystals that the density of possible atomic positions is larger than the density of finally occupied positions (phason freedom). The occupied positions are selected by the Monte Carlo process according to both energetical and entropical preferences; therefore, this is not the occupation of a fixed lattice as in most of the Monte Carlo growth simulations of crystals⁵ and quasicrystals.⁸ Instead, two types of local atomic configurations are allowed (icosahedral and dodecahedral) which leave more freedom for structure formation. The final quasilattices and, hence, atomic surfaces of grown quasicrystals (see Fig. 5), result from the growth process; it is possible to change them changing the interatomic potential, to introduce more or less defects, etc. so that the grown quasicrystal might better fit experimental diffraction patterns. It should be emphasized that our growth algorithm is completely three-dimensional; we use the perpendicular components only for characterization of grown quasicrystals.

The growth (melting) rate is governed by the difference between atomic energies in the liquid and on the surface, as well as by kT_{melt} . On the average, the final positions are occupied only after many attempts (see Fig. 4); this is typical of real growth from the liquid state when an atom is finally fixed in the solid phase after 10^3 to 10^6 adsorptions and desorptions.³² It is difficult to simulate such a slow growth within reasonable computer time. Hence, in our simulations, the growth run so fast (less than 10^3 attempts per atom) that it corresponds rather to a quenching process or to rapid melting (notice that the number of Monte Carlo attempts is larger than the number of adsorptions and desorptions because not all of the attempts are successful). In this range the growth (melting) rate is approximately proportional to $\Delta\mu$, hence to amount of supercooling (superheating). Within a certain interval around the melting point, the growth (melting) should be extremely slow because of the energy barriers. In this respect quasicrystals behave even worse than crystals because they have an inhomogeneous hierarchical structure. It is practically impossible to overcome these barriers within the Monte Carlo simulations (that is true even of the barriers between small clusters considered in Sec. V).

Traditionally, the cluster concept has been very popular in quasicrystal science. The clusters are usually considered either as ready-made building blocks²⁻⁴ or as a result of a hierarchical organization of quasicrystals.³¹ We have demonstrated here that different types of clusters may result from local growth with spherically symmetrical Friedel potentials. The clustering reveals itself during growth and especially during melting; it seems to be a result of the difference in energy between different atomic positions. Indeed, in average, the positions with a higher energy (which are at the periphery of the acceptance domain) melt first. This is confirmed by our observation that the positions on the growing

(melting) surface have a smaller mean-square perpendicular size. In real alloys, this should result in a difference between bulk and surface concentrations of different chemical elements: the surface should be enriched by those elements which are closer to the center of the atomic surface in perpendicular space.

Usually, in our grown quasicrystals, the so-called “tears,” which were typical of earlier models,^{2,3} are not found, except if the growth process is so bad that the perpendicular space size of the cluster is rapidly expanded; then a few tears do appear, that is to say, some short interatomic distances acquire wrong values that violate both DLO and ILO. A “bad growth process” means either an interatomic potential without oscillations or a very high growth rate. In fact, the average size in perpendicular space always increases

with the real-space size; this means that the growing quasicrystal contains more and more phason defects. However, in our growth model, this increase is much less than in the best previous models^{3,4} and this model has a potential for further improvement.

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