A simple theoretical model for evaluating the ability to form a single crystal*

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A simple theoretical model proposed recently to evaluate the ability of bulk materials to form single crystals is further tested via vast molecular dynamics simulations of growth for fcc (Ni, Cu, Al, Ar) and hcp (Mg) crystals, especially applied to the growth of bcc (Fe) crystal, showing that the validity of the model is independent of crystal types and the interaction potentials of the constitute atoms.

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Novel properties of newly designed materials are widely predicted via modern physics theory, but it is difficult to estimate the ability for given chemical constitutes to form a desired atomic structure belonging to a new type of material. For example, C_3N_4 crystal (for the α-, β- and c- phase) was predicted to be as stiff as diamond more than ten years ago,[1,2] yet it is impossible to grow the grains of up to ten micrometres.[3,4] Clearly a problem arises whether the ability for C_3N_4 to form single crystal is higher than that for diamond or not. In fact, materials differ considerably in their crystallising ability. For instance, single-crystal quartz of several tens of centimetre in size can be easily produced in common experiments, but it is difficult to grow diamond grains and C_{60} or C_{70} single crystal with macro size.[5−9] Accordingly, a theory is highly desired to evaluate the abilities for materials to form single crystals.

In molecular dynamics (MD) simulations of argon crystal growth, we found a clue to the problem. Figure 1(a) shows an epitaxial structure of argon solid drawn from our MD simulations, which started from a piece of Ar melt sited on a seed of Ar crystal with a perfect structure. In the simulations, all the atoms were allowed to relax according to classical mechanics, with the seed crystal attached to a heat bath at about 40 K. As shown in Fig. 1(a), when the melt atoms roughly grouped into about ten layers separated by the distance between perfect (111) faces, the atoms in each melt layer did not occupy the right lattice sites. We guessed that the melt atoms felt a deeper potential valley in the z direction, while shallower ones in the x–y plane since the atoms were trapped first in the z direction during the growth process. Indeed, the depth of the potential valley (P_z) which a single Ar atom felt in the z direction, is much larger than the one (P_s) that a single Ar atom felt in the x–y plane (Fig. 1(b)). It is clear that the crystallizing process is closely related to these two potential valleys.

Inspired by this fact, we recently proposed a concept of condensing potential (CP) to evaluate the ability for materials to form a single-crystal structure.[10] To calculate CP we constructed a crystal surface and place a probe atom on it to test the surface potentials (Fig. 1(c)). When the probe atom approaches the surface in the z direction, it experiences a potential valley with depth, P_z, and when the atom diffuses on the surface, it experiences another potential valley with depth denoted by P_s. Intuitively, if both P_s and P_z are large, the surface will have a great ability to form a single-crystal structure; if either P_z or P_s equals zero, the material will tend to form an amorphous structure. Thus, we define the condensing potential (CP)

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as

$$\mathrm{CP} = P_z \times P_s. \tag{1}$$

It is reasonable to speculate that materials with larger CP should grow with fewer defects and thereby tends to form larger single-crystal grains. Note, since there exist infinite directions in the x–y plane, corresponding to various potential valleys, the shallowest one is chosen for the calculation of CP.

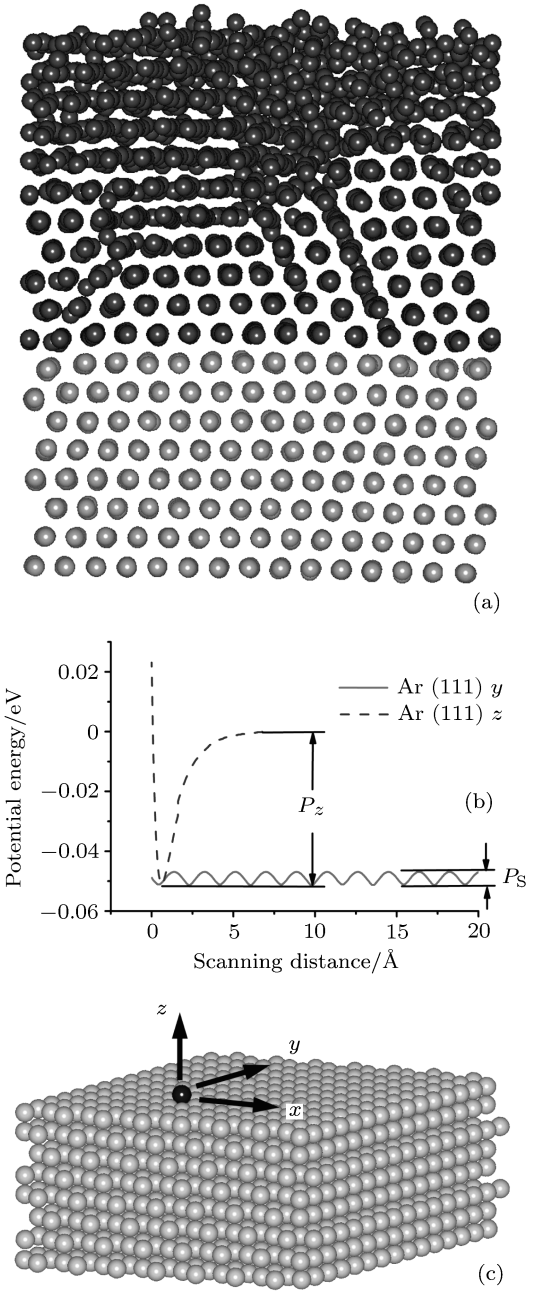


Fig. 1. (a) Snapshot of Ar crystal growth from the (111) face, with dark and light balls representing the melt and the material seeds, respectively; (b) potentials felt by a probe Ar atom over the (111) surface in y and z directions, and (c) schematic diagram for scanning the potential field near the surface (1 Å=0.1 nm).

In order to test this speculation, we preformed MD simulations of crystal growth, which has been widely used to study the crystallizing process,[11−13] and introduced another concept, fault degree (FD), to evaluate the quality of the grown crystal

$$\mathrm{FD} = (E_0 - E)/E_0, \tag{2}$$

where E and E_0 are, respectively, the total potential energies for the grown crystal at the temperature of 0 K and a perfect crystal at 0 K composed of the same number of atoms as that in the grown crystal. Since E increases with the number of defects, larger FD presents more defects formed in the grown crystal, and therefore FD should decrease monotonically with CP increasing.

Considering that the CP model was tested in our previous work via small models of MD simulation, limited to fcc(Ni, Cu, Al, Ar) and hcp (Mg) crystals, we employed in this work larger MD models which contain nearly twice the atoms of the previous one[10] in number to further test the CP model for Ni, Cu, Al, Ar, Mg crystals, especially for bcc (Fe) crystal. These larger simulation models should be capable of reducing some undesired effects, such as the boundary effects in the small models, and would provide more convincing information about the crystal growth.

Firstly, we performed MD simulation of the crystal growth on the (100), (110) and (111) faces of Ni, Cu, Al, Ar crystals, and on the (0001) face of Mg crystal. Sizes of the new models on different faces are shown in Table 1. The simulation and the calculation of FD and CP are similar to the ones in our previous work with the same Tight–Bonding interaction potentials.[14,15] To obtain a robust estimation, each FD was averaged over 20 independent simulations.

The newly calculated FDs compared with the previous ones are shown in Table 2. It is seen from Table 2 that all the new FDs are significantly larger than those from our previous small model, indicating that the quality averaged over the large model turn worse significantly. For example, the FD increases of Cu(111), Cu(100) and Cu(110) are 29.6%, 7.3% and 11.9% respectively, while the FD of Ar increases more. This is natural since earlier formed defects would be amplified in the following growth, and the larger system with longer growth period provides more chances for the defects to expand. That is why it is more difficult to grow large crystal grains.

Table 1. Details of simulation models.

structure	face	periodic boundary	arrangement of layers	layers of the seeds	atoms of melt	total atoms
fcc	(111)	2d(x, y)	18×18	8	2268	4860
(Ni,Cu,Al,Ar)	(110)	2d(x, y)	18×18	8	2268	4860
	(100)	2d(x, y)	26×13	8	2366	5070
hcp(Mg)	(0001)	2d(x, y)	18×18	8	2268	4860
bcc(Fe)	(100)	2d(x, y)	18×18	8	2268	4860
	(110)	2d(x, y)	20×15	8	2100	4500
	(111)	2d(x, y)	20×15	8	2100	4500

Table 2. Details of newly calculated FDs and the previous ones.

material(face)	FD1(present work)	FD2(Ref[10])	FD1/FD2
Ni(100)	3.01×10^{-4}	2.00×10^{-4}	1.501
Ni(110)	7.50×10^{-4}	2.69×10^{-4}	2.786
Ni(111)	0.00246	0.00185	1.329
Cu(100)	0.00161	0.00150	1.073
Cu(110)	0.00151	0.00135	1.119
Cu(111)	0.00242	0.00187	1.296
Al(100)	0.00186	0.00167	1.111
Al(110)	0.00199	0.00176	1.131
Al(111)	0.00320	0.00267	1.198
Ar(100)	0.00639	0.00434	1.473
Ar(110)	0.01368	0.00893	1.531
Ar(111)	0.01614	0.01191	1.355
Mg(0001)	0.00500	0.00378	1.323

Since CP is independent of system size, it is reasonable to compare the newly obtained FDs with our previously obtained ones[10] in the same CP–FD figure (Fig. 2).

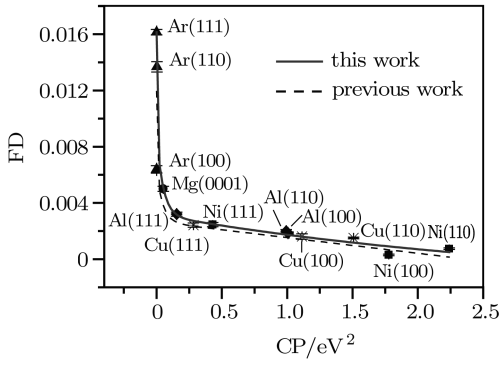


Fig. 2. FD–CP curves from larger systems for the newly grown fcc crystals (Ni, Cu, Al and Ar) from (100), (110) and (111) faces, hcp crystal (Mg) from (0001) face (solid line) and the previous one[10] (dash line).

It is clear from Fig. 2 that the new CP–FD curve shares the same trend with the previous one, which shows that FD decreases monotonically with CP increasing. So this relation should be independent of system size and further tests with more larger MD simulation models are unnecessary. This result strongly confirms the conclusion that CP can be used to evaluate the ability for materials to form a single crystal.

Considering that the above work is limited to fcc and hcp crystals, we applied CP model to bcc crystal iron. All the calculations on iron were based on the embedded atom method (EAM) potential,[16,17] which consists of a pairwise part and a local density part and is given as

$$U = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \varphi(r_{ij}) + \sum_{i=1}^{N} \varphi(\rho_i), \tag{3}$$

where i and j are atomic labels, N is the total number of atoms, r_{ij} is the separation between atoms i and j, and

$$\rho_i = \sum_j \psi(r_{ij}). \tag{4}$$

All functions are represented as a sum of basis func-

tions each

$$\varphi(r) = \sum_{k=1}^{n^{\varphi}} a_k^{\varphi} \varphi_k(r), \tag{5}$$

$$\psi(r) = \sum_{k=1}^{n^{\psi}} a_k^{\psi} \psi_k(r), \tag{6}$$

$$\phi(\rho) = \sum_{k=1}^{n^{\phi}} a_k^{\phi} \phi_k(\rho). \tag{7}$$

The EAM potential faithfully reproduces the lattice constant, the liquid density and the structure factor of iron. Moreover, it predicts the melting point to be 1772 K, consistent with the experimental value 1812 K.[18] The optimal temperature for crystal growth may be close to $0.6T_{\rm m}$ ($T_{\rm m}$ denotes the melting point)[10] and our previous MD growth simulations of Ni, Cu, Al, Ar and Mg crystals were all performed at $0.6T_{\rm m}$. For a reasonable comparison, a similar simulation and calculation on Fe crystal should also be performed for $0.6T_{\rm m}$, i.e. 1100 K. At 1100 K, however, the Fe crystal will experience a phase transition from bcc to fcc. As a compromise, 900 K was chosen in our study on Fe.

For fcc crystals (Ni, Cu, Al, Ar), the CPs show a sequence of $\mathrm{CP}_{110} > \mathrm{CP}_{100} > \mathrm{CP}_{111}$, while for bcc Fe, the sequence changes into $\mathrm{CP}_{111} > \mathrm{CP}_{100} > \mathrm{CP}_{110}$. Since CP_{110} (0.875 eV^2) is much smaller than CP_{100} (3.53 eV^2) and CP_{111} (4.59 eV^2) for the Fe crystal, it is expected that the crystals grown on (110) face would contain the most defects, while the grown crystal on (111) face would have the fewest ones. Compared with the CPs of fcc crystals, the CPs of iron are on average much larger than those of the others. As an example, the CPs of Ni (111) and Al (111) are 0.430 eV^2 and 0.153 eV^2, respectively, which are significantly smaller than all the CPs of Fe crystal. It is indicated that Fe crystal grown from all the three faces would contain fewer defects than those from Ni (111) and Al (111) faces.

To test the predictions based on the CPs, the crystal growths of iron on surfaces (100), (110) and (111) were further investigated by MD simulations. The model consisted of a crystal seed and a piece of melt located on a given face of the seed. Sizes of the three models on different surfaces are shown in Table 1. Periodical boundary conditions in lateral ($x - y$) directions were imposed on all the models. In the MD simulation, temperatures of the seed and the melt were initially set to be 900 K and 1900 K, respectively. We controlled the simulation temperature via resetting velocities of the atoms in the bottom layer of the seed, which was considered to be in contact with a thermal bath.[19] The system was allowed to relax for ∼100 ps to establish a solid–liquid interface. Then the whole system was relaxed at 900K until all the melt grew into crystal completely. Finally, a damped trajectory method[20,21] was used to cool the system down to 0 K to calculate the FD of the system. As we did previously, each FD was averaged over 20 independent simulations.

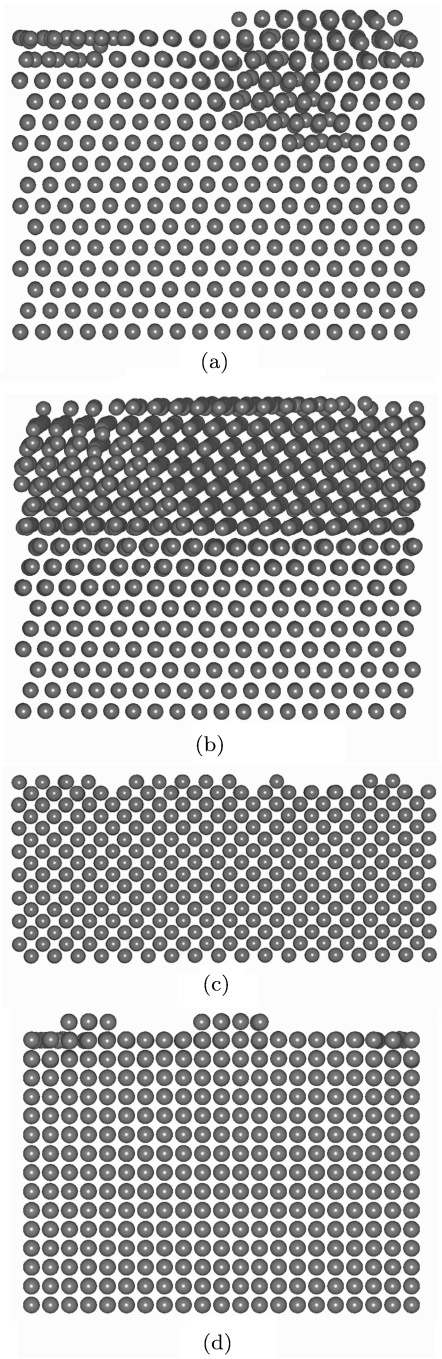


Fig. 3. Front views of (111) face growth for Ni (a), Al (b) and (100) face (c) and (110) face (d) for bcc-structured Fe.

The FDs of iron on (110), (100) and (111) faces are found to be 0.00130, 0.00124, and 0.000693, respectively, i.e. $FD_{110} > FD_{100} > FD_{111}$, which is coincident with the sequence $CP_{111} > CP_{100} > CP_{110}$. It should be mentioned that the CP sequence is consistent with that of surface free energies of bcc crystals,[22] and it is well known that crystal growth is easier on the surfaces of higher free energy, which justifies our model from another point of view. Moreover, all the FDs of Fe are smaller than those of Ni and Al on (111) face, which is consistent with the CP predictions. In Fig. 3 we show some representative results in our simulations. It is seen that structures grown on (100) and (110) faces of Fe contain less defects than those on Ni (111) and Al (100) faces.

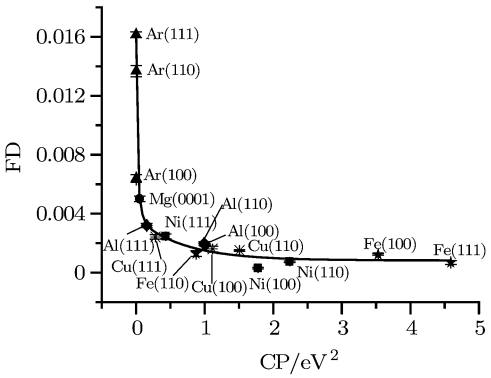


Fig. 4. FDs and CPs of the bcc-structured Fe crystal from (100), (110) and (111) faces fitted into an FD–CP curve.

All the CPs and FDs for bcc (Fe), fcc (Ni, Cu, Al, Ar) and hcp (Mg) crystals can be well fitted into a CP–FD curve shown in Fig. 4, indicating that the relationship between CP and FD is independent of crystal type. This relation should be also independent of potential function, because the EAM potential for Fe is very different from the tight-binding potentials for Ni, Cu, Al and Mg.

In summary, we justify the validity of the CP model by simulating the crystal growths of Ni, Cu, Al, Ar, Mg and especially Fe, the bcc structured material with larger MD simulation models, extending this CP model to a wider range of materials. Based on the CP–FD curve, a prediction procedure may be set up as follows. Calculate CPs of the newly designed materials and find out its corresponding FD from the CP–FD curve, and thus whether the ability to form single crystals of the new materials is higher or lower than the crystallizing ability of Ni, Cu, Al, Ar, Mg or Fe can be judged. Since calculation of the CP is simple and can be realized by general *ab initio* package, the predictions could be implemented conveniently.

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