The displacement field associated with the freezing of a melt and its role in determining crystal growth kinetics

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The atomic displacements associated with the freezing of metals and salts are calculated by treating crystal growth as an assignment problem through the use of an optimal transport algorithm. Converting these displacements into timescales based on the dynamics of the bulk liquid, we show that we can predict the activation energy for crystal growth rates, including activation energies significantly smaller than those for atomic diffusion in the liquid. The exception to this success, pure metals that freeze into face-centered cubic crystals with little to no activation energy, are discussed. The atomic displacements generated by the assignment algorithm allows us to quantify the key roles of crystal structure and liquid caging length in determining the temperature dependence of crystal growth kinetics.

Significance

We demonstrate that an accurate estimation of the displacements associated with the transformation of liquid into crystal is necessary to explain the striking variations in the temperature dependence of the addition rate of liquid atoms to the growing crystal interface during freezing. An assignment algorithm, adapted from operations theory, is shown to provide a good estimate of these atomic displacements. As the assignment algorithm requires only initial and target locations, it is applicable to all forms of structural transformations. In resolving a fundamental feature of the kinetics of freezing, a phenomenon cable to all forms of structural transformations, this paper also provides the tools to open lines of research into the kinetics of structural transformation.

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the displacement field (Fig. 2B) was found to provide a reasonable
prediction of the observed activation energy for crystal growth.

The existence of ordered interfacial ground states—the observa-
tion that formed the basis of the analysis in refs. 11 and 12—is
not the norm in crystal growth. In ref. 12 Fe and ZnS were shown
to not order at the interface during energy minimization. The
(111) face of a Lennard-Jones crystal is another example (11). We
propose that the majority of materials do not exhibit ordering on
minimization. Clearly, we cannot simulate every system. Our claim
is based on the generic experimental observations of activated
control of crystal growth (13) for materials other than pure metals
and some simple salts. Activation indicates an energy barrier
for the ordering process at the interface and, hence, strongly
implies the inaccessibility of the crystal from the liquid by any
minimization algorithm that imposes a continuous decrease in
the potential energy.

Transformation Displacement Fields as a Problem of
Optimal Transport

If energy minimization does not provide a mapping from liquid
to crystal at the interface, we must find another way of defining
the transformation displacement field for an arbitrary crystal
growth problem. In general, the displacement field corresponds
to an assignment mapping where each liquid atom is assigned
to a crystal site. The total number of distinct possible ways of
assigning \( N_l \) liquid atoms to \( N_c \) crystal sites (both regarded as
distinguishable by virtue of their locations) is
\[
\frac{N_c!}{(N_c - N_l)!}
\]
where we have assumed that \( N_c > N_l \) (14). The displacement fields for
most of these possible assignments will be of no physical signifi-
cance. We propose that the set of displacements of interest is that
with the minimum average displacement. While this minimal field
may not represent the path taken by any given ordering trajectory,
it does provide a lower bound on the characteristic transformation
displacement. This means that if this minimal length exceeds the
threshold length obtained from the liquid cage length, then we can
be confident that the associated freezing transition is diffusional in
character.

The problem of assigning atoms to crystal sites to minimize the
mean displacement is an example of a problem well known in
linear programming where it is called the optimal assignment
problem or, more generally, the optimal transport problem (15).
Transport problems occur frequently in operations research—
matching workers to tasks, examinations to time slots, etc. A
widely used solution is the Hungarian Algorithm (HA) described
by Kuhn in 1955 (16). We have implemented the HA for the
crystal growth problem as follows. 1) All calculations have been
carried out with a particle-to-site ratio, \( N_l/N_c \sim 0.6 \). 2) The
reported displacements are the components in the interfacial
plane only. 3) The assignment is applied to atoms in the liquid
that lies within two lattice spacings of the interface position.

![Fig. 1. The change in a configuration corresponding to crystal and liquid as a result of the minimization of the potential energy for (A) Cu (111) and (B) Fe (110). The position of the interfaces in the initial and minimized configurations are indicated by vertical red dashed lines. Note that the Cu (111) interfaces advance while the Fe interfaces do not.](https://www.pnas.org/cgi/doi/10.1073/pnas.1915806117)

![Fig. 2. (A) The distribution of displacements associated with the crystal formation from the interfacial liquid atoms arising from the minimization of the potential energy in Cu (111) at \( T = 1,100 \) K. The vertical dashed line indicates the median value \( d_m \). The distribution can be well described by a log-normal distribution (blue curve). (B) Plots of the MSD \( \langle \Delta r^2(t) \rangle \) vs. \( t \) in liquid Cu (111) showing the extraction of the \( T \)-dependent timescale \( \tau \) associated with the MSD \( \langle d^2 \rangle \). The different curves correspond to different temperatures with the larger value of MSD associated with a larger value of \( T \) (as indicated).](https://www.pnas.org/cgi/doi/10.1073/pnas.1915806117)
The intrinsic crystal growth rate is the rate at which the crystal front propagates when unrestrained by heat or concentration diffusion. It is the growth rate controlled by the kinetics of microscopic ordering alone. The temperature dependence of these rates allows us to empirically distinguish diffusive from displacive transformations based on whether the associated activation energy is equal to or less than that for diffusion in the bulk liquid. We shall apply the standard resolution (17) of the growth rate \( v(T) \) into a thermodynamic term and a kinetic coefficient \( k(T) \) using

\[
v(T) = k(T)[1 - \exp(\Delta \mu / k_B T)],
\]

where \( \Delta \mu \) is the chemical potential difference and \( k_B \) is the Boltzmann constant. Estimating the chemical potential difference as \( \Delta \mu = (T - T_m) \frac{\Delta h}{\Delta v} \) (with \( T_m \) being the melting point and \( \Delta h = h_{liq} - h_{cryst} \), with \( h \) being the enthalpy per particle of the respective phase), Eq. 1 allows us to extract the kinetic coefficient from the calculated rates \( v(T) \). In this paper we shall analyze the crystal growth kinetics of the following model systems. As examples of a metal and a salt whose crystal growth shows little to no activation barrier, we include Cu and NaCl. As examples of a metal and a salt whose crystal growth shows significant activation (and no sign of an ordered interfacial ground state), we include Fe and ZnS. Finally, we include a family of binary Lennard-Jones equimolar mixtures that freeze into a cubic CsCl crystal. This mixture is based on a model due to Kob and Andersen (KA) (18) that has been studied extensively in the context of glass formation. These mixtures have been included as their crystal growth kinetics provide a continuous range of activation energies through a small adjustment of their interaction (as described below). The metals are modeled using an embedded atom model potential due to Foiles et al. (19) and Mendeleev et al. (20), NaCl is modeled using the Tosi–Fumi potential (21), and ZnS is modeled using a potential due to Grünwald et al. (22). The binary Lennard-Jones mixtures \( A_{50}B_{50} \) are modeled with the following interaction potential:

\[
\phi_{ij}(r) = 4\varepsilon_{ij} \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6},
\]

where the masses are equal, \( \varepsilon_{ij} \) and \( \sigma_{ij} \) are the depth of the potential well between particle \( i \) and \( j \) and finite distance at which the potential (first) vanishes, respectively, \( \varepsilon_{AA} = 1.0, \varepsilon_{AB} = 1.5, \varepsilon_{BB} = 0.5 \) and \( \sigma_{AA} = 1.0, \sigma_{BB} = 0.88 \). The final parameter \( \sigma_{AB} \) (which equals 0.8 in the original KA model) is allowed to vary over the range 0.76 \( \leq \sigma_{AB} \leq 0.84 \). The crystal structures and melting points for these models are provided in Table 1. The crystal growth rates \( v(T) \) were calculated using molecular-dynamics simulations from the LAMMPS (23) set of algorithms. As described previously (11, 12), a uniform temperature is maintained throughout the run and the density is allowed to adjust through the

(A detailed explanation of these choices in the implementation of the HA is provided in SI Appendix.) An example of the displacement field for an interfacial plane of the Cu crystal is shown in Fig. 3. We note the presence of collective motions arising solely from the particle exclusion associated with the requirement of single occupancy of crystal sites.

**Assignment Displacements and the Temperature Dependence of Crystal Growth Rates**

Table 1. The crystal structure, melting points \( T_m \) and parameters associated with the kinetics of crystal growth and liquid diffusion for the model systems

| Crystal structure | \( T_m \) | \( k(T_m) \) | \( \varepsilon_D \) | \( E_u \) | \( E_a \) |
|-------------------|---------|---------|---------|--------|--------|
| Cu                | 1,275 K | 214 m/s | 0.336 eV| 0.04 ± 0.006 eV | 0.13 ± 0.02 eV |
| NaCl              | 1,074 K | 273 m/s | 0.275 eV| 0.08 ± 0.01 eV | 0.06 ± 0.024 eV |
| Fe                | 1,775 K | 1,012 m/s | 0.557 eV| 0.35 ± 0.05 eV | 0.25 ± 0.035 eV |
| ZnS               | 1,750 K | 130 m/s | 0.566 eV| 0.40 ± 0.05 eV | 0.33 ± 0.045 eV |
| \( AB (\sigma_{AB} = 0.76) \) | CsCl | 0.687 (kg/\( \varepsilon_{AA} \)) | 0.114* | 4.22 (\( \varepsilon_{AA} \)) | 3.8 ± 0.31 (\( \varepsilon_{AA} \)) | 3.44 ± 0.41 (\( \varepsilon_{AA} \)) |
| \( AB (\sigma_{AB} = 0.80) \) | CsCl | 0.772 (kg/\( \varepsilon_{AA} \)) | 0.165* | 3.74 (\( \varepsilon_{AA} \)) | 1.53 ± 0.08 (\( \varepsilon_{AA} \)) | 1.3 ± 0.12 (\( \varepsilon_{AA} \)) |
| \( AB (\sigma_{AB} = 0.82) \) | CsCl | 0.77 (kg/\( \varepsilon_{AA} \)) | 0.132* | 3.48 (\( \varepsilon_{AA} \)) | 1.7 ± 0.11 (\( \varepsilon_{AA} \)) | 2.1 ± 0.27 (\( \varepsilon_{AA} \)) |
| \( AB (\sigma_{AB} = 0.84) \) | CsCl | 0.752 (kg/\( \varepsilon_{AA} \)) | 0.12* | 3.29 (\( \varepsilon_{AA} \)) | 2.4 ± 0.13 (\( \varepsilon_{AA} \)) | 2.5 ± 0.36 (\( \varepsilon_{AA} \)) |

Presented are \( k(T_m) \), the crystal growth kinetic coefficients (Eq. 1) at \( T_m \), the activation energies \( E_D \) and \( E_a \) for diffusion and \( k(T) \), respectively, and \( E_u \), estimated value of the growth rate activation energy based on the assignment analysis.

*The kinetic coefficients \( k(T_m) \) for the AB mixture are in units \( \sqrt{\varepsilon_{AA}/m} \). The crystal-face studies here are Cu (111), Fe (110), NaCl (100), and ZnS (100), and the (100) surface of the body-centered CsCl crystal in the case of the KA mixtures.
inclusion of free liquid. These details, along with the crystal growth rates $v(T)$, are provided in SI Appendix. For FCC, we have calculated growth along the $<111>$ direction, and for body-centered cubic (BCC) structure, the growth direction investigated is along the $<110>$ direction. The growth directions of the rocksalt crystal for NaCl and the wurtzite for ZnS are both along the $<100>$ direction. In the case of the CsCl crystal, we have considered growth along the $<100>$ direction. Details of the simulation protocol along with the tabulated $v(T)$ vs. $T$ data for all of the models are provided in SI Appendix.

In Table 1, we present the activation energy $E_a$, obtained empirically by fitting the rate coefficient $k(T)$ [obtained from $v(T)$ using Eq. 1] to an Arrhenius function, $k(T) = k_0 \exp \left( \frac{-E_a}{k_B T} \right)$, where $k_0$ is the pre-exponential factor, and $E_a$ is the energy activation energy. For comparison, we also present the activation energy $E_D$ for self-diffusion in the homogeneous liquid, obtained by an Arrhenius fit to the self-diffusion coefficient $D_0$ of the form $D \propto \exp \left( \frac{-E_D}{k_B T} \right)$. The generic signature of “diffusionless” growth is $E_a/E_D$ significantly smaller than 1.0, a situation that describes the cases of Cu and NaCl. Fe and ZnS, in contrast, exhibit a growth coefficient with an activation energy similar to that of atomic diffusion in the liquid while the modified KA mixtures exhibit values over the range $0.41 \leq E_a/E_D \leq 0.91$. How do we account for this variety of degrees of activated control in crystal growth? We propose that the distribution of displacements generated by the optimal assignment algorithm, HA, provides the essential information we need. To translate the displacements into timescales we use the calculated mean-squared displacement (MSD) of the bulk liquid as shown in Fig. 4 where a displacement $d$ is translated into a time $t$ using the relation $d^2 = \langle \Delta r^2(t) \rangle$. The temperature dependence of this relation arises from the temperature dependence of the liquid $<\Delta r^2(t)>$ (Fig. 4). Having generated a distribution of timescales $P(t)$ we calculate the average rate $1/\tau$ over this distribution and extract our predicted crystal growth activation energy $E_a$ by fitting the temperature dependence of $1/\tau$ to an Arrhenius temperature dependence (SI Appendix). The resulting values for $E_a$ are reported in Table 1.

We find, as shown in Fig. 5, that the estimate of the activation energy $E_a$ for crystal growth based on the distribution of displacements generated by the assignment algorithm provides a reasonable prediction of $E_a/E_D$ and, hence, the degree of activated control of the crystal growth kinetics. A clear exception to this success is Cu where the assignment analysis results in a significant overestimate in the barrier to growth. It is likely that this represents a general limitation of the assigned displacements. When $E_a$ <<1.0, the dynamics of growth is dominated by collective vibrations about the crystalline ground state in the interface which is not adequately described by simply assigning atoms to sites based on minimizing the mean displacement. A more appropriate approach for this limiting behavior is to use the characteristic vibrational frequency of the bulk crystal as proposed in ref. 11.

The general success of the freezing displacement fields, as generated by the assignment analysis, in predicting the degree of activated control of crystal growth kinetics represents the major result of this paper. In using the liquid MSD data to map lengths to timescales we are following the same reasoning used in the earlier theories of the kinetic coefficient for crystal growth. Where we deviate from these earlier approaches is in providing a more nuanced measure of the displacement lengths associated with ordering a liquid. The Wilson–Frenkel theory of crystal growth assumes that $E_a/E_D = 1.0$. The marked deviations from this “classical” theory in Fig. 5 are the direct result of identifying length scales small enough to access dynamics that show little activated control. While the lengths we find using the optimal transport analysis may differ by only a small amount from those assumed in the earlier studies (11, 12), the difference can be physically significant and give rise to very large differences in both the temperature dependence of crystal growth rates as well as its absolute magnitude.

**Mapping to Alternate Crystal Structures: Polymorphs and Substitutionally Disordered Crystals**

We have reported that Cu freezes into an FCC crystal by a diffusionless process but the freezing of Fe to a BCC structure is diffusional. What is the origin of the difference? Is it some property of the liquid or does the difference lie with the different crystal structures? The optimal transport analysis provides a useful means of directly addressing question such as this since it allows us to select any target crystal structure we choose. If Fe was to freeze into the FCC structure, as opposed to BCC, how
would the distribution of displacements and, hence, the nature of the transformation change? The assignment analysis allows us to address this question since we are free to select the target crystal to map the liquid particles to when generating the displacement distribution. The value of $E_a/E_D$ for Fe mapped to the FCC crystal is 0.46, essentially the same as the value 0.45 when mapped to the BCC structure. We can ask similar questions of the molten salts. In Table 2 we present the values of $E_a/E_D$ for the interfacial liquid NaCl and ZnS when mapped to rocksalt and wurtzite structures, both compositionally ordered and compositionally random.

Referring to Table 2, we find that NaCl does exhibit a significantly smaller value of $E_a/E_D$ when mapped to rocksalt than when mapped to wurtzite. ZnS, on the other hand, behaves like Fe and shows little difference between the two possible crystal targets. We conclude that the manifestation of significant diffusive control, i.e., $E_a/E_D > 0.4$, does not depend on the crystal structure but is a consequence of the liquid. It appears that when the barrier to growth is particularly small (as in the case of NaCl), the choice of crystals may play a role in influencing the temperature dependence of growth. The results for the random crystals in Table 2 showed little variation for the values of $E_a/E_D$ for the compositionally ordered crystal. This is a surprising result as the observation of accelerated growth rates for disordered plastic crystal (24) would lead us to expect that disorder in the crystal would lead to faster kinetics. Clearly this is a question worth further study.

Conclusions

We have demonstrated that crystallization from the melt can occur via crystal growth with an activation energy that can take on a value $0 \leq E_a \leq E_D$ depending on the magnitude of the displacements associated with the transformation. We have introduced the HA, from optimal transport theory, to provide a general mapping of liquid atoms to crystal sites and so generate the transformation displacements between dense phases. We have shown in this paper that these displacements, when translated into timescales using the dynamics of the bulk liquid, provide a good prediction of the degree of activated control of crystal growth. The crucial insight into understanding crystallization kinetics is that, when dealing with particle displacements on the order of the cage length of the liquid, very small changes in displacement can shift the dynamics from ballistic control to diffusive control. This means that understanding the kinetics of crystallization requires an accurate determination of the scale of movement needed for the transformation.

The exception to the success of the assignment analysis are those materials that exhibit very small or no activation barrier to crystal growth. The pure FCC-forming metals belong to this general group. As shown in Fig. 5 and Table 1, the assignment analysis significantly overestimates $E_a$ for Cu. Previously (11), we have argued that, in the absence of a barrier, the process of crystallization more closely resembles a complex collective phonon mode than the incoherent motion that characterizes liquid dynamics. It is not surprising, then, that the simple minimization condition that defines the displacements generated by the HA would be a poor estimate of the coherent motions involved in ordering when the local potential energy minimum is crystalline. For these materials, the characteristic frequency of the crystal vibrations provides a better estimate of the magnitude of the ordering coefficient $k$.

Previous studies have observed anisotropy in crystal growth rates. In the case of the Lennard-Jones (LJ) FCC crystal, the (111) surface exhibits activated growth while the (100) surface grows without any apparent barrier (25, 26). Applying the assignment analysis to these two surfaces, we find only a small decrease in the predicted activation energy for growth estimated for LJ(100) surface relative to that for the LJ(111) surface, 1.6e and 1.8e, respectively. This result for LJ(100) surface is consistent with the failure of the assignment analysis, already noted, when applied to barrierless growth such as that of Cu. We leave a more extensive study of the origin of anisotropy in crystal growth kinetics for future study.

Our introduction of transformation displacements and the HA for their calculation opens up lines of study of crystallization kinetics based on measures of configurational proximity (i.e., the magnitude of the transformation displacements) between a disordered and ordered structure. As demonstrated here, a researcher has complete freedom in the choice of the target structure. Polymorphs, substitutional disorder, or orientational disorder (in the case of molecules) could be considered in exploring how different aspects of structure influence the characteristic displacements atoms or molecules must undergo in a phase transformation. The optimal transport analysis can also be extended to transformation from one disordered structure to another in bulk liquids, quantifying the kinetic accessibility of different distinct configurations in a liquid. A number of these questions are the subject of current research.

Data Availability Statement. All the data supporting the findings of this study are available within this paper and the SI Appendix.

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Table 2. The ratio $E_a/E_D$ for the assignment of the interfacial NaCl and ZnS to the rocksalt and wurtzite structures

|                | Rocksalt (random) | Wurtzite (random) |
|----------------|------------------|-------------------|
| NaCl           | 0.247(0.229)     | 0.403(0.376)      |
| ZnS            | 0.605(0.593)     | 0.591(0.57)       |

The lattice spacings of the target crystal structures were adjusted to match the cation–anion contact distance (SI Appendix). The values in brackets are for target crystals with random composition on the lattice sites.
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