Influence of string-like cooperative atomic motion on surface diffusion in the (110) interfacial region of crystalline Ni

Hao Zhang,^{1,a)} Ying Yang,¹ and Jack F. Douglas^{2,a)}

¹Department of Chemical and Materials Engineering, University of Alberta, Alberta T6G 2V4, Canada

²Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

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Although we often think about crystalline materials in terms of highly organized arrays of atoms, molecules, or even colloidal particles, many of the important properties of this diverse class of materials relating to their catalytic behavior, thermodynamic stability, and mechanical properties derive from the dynamics and thermodynamics of their *interfacial regions*, which we find they have a dynamics more like glass-forming (GF) liquids than crystals at elevated temperatures. This is a general problem arising in any attempt to model the properties of naturally occurring crystalline materials since many aspects of the dynamics of glass-forming liquids remain mysterious. We examine the nature of this phenomenon in the “simple” case of the (110) interface of crystalline Ni, based on a standard embedded-atom model potential, and we then quantify the collective dynamics in this interfacial region using newly developed methods for characterizing the cooperative dynamics of glass-forming liquids. As in our former studies of the interfacial dynamics of grain-boundaries and the interfacial dynamics of crystalline Ni nanoparticles (NPs), we find that the interface of bulk crystalline Ni exhibits all the characteristics of glass-forming materials, even at temperatures well below the equilibrium crystal melting temperature, T_m . This perspective offers a new approach to modeling and engineering the properties of crystalline materials. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4908136>]

INTRODUCTION

It is a well-known quip by Wolfgang Pauli that “God made the bulk; surfaces were invented by the devil”.¹ Many properties and processes important for industry and living systems derive from thermodynamic and dynamic properties of interfaces. For example, interfacial mobility is central to fundamental processes underlying catalysis, crystal nucleation and growth, interfacial transport, corrosion, fracture, etc. Specifically, the industrial fabrication of thin smooth films by epitaxial growth for materials applications in the electronics industry and rough films for catalysis applications,² the controlled growth of carbon nanotubes and nanofibers from nanoparticle catalysts using plasma enhanced chemical vapor deposition³ and the development of electrolyte materials for efficient fuel cells^{4,5} provide concrete examples in which the control of interfacial mobility is key to materials manufacturing and discovery. Even in the case of crystalline materials, however, it is extremely difficult to characterize the structure and dynamics of interfaces from both experimental and theoretical standpoints and this difficulty often fundamentally limits our capacity to design materials with desired properties. In many ways, this is a fundamental weak link in the chain of materials modeling.

In the present work, we investigate the relatively simple problem of characterizing the interfacial dynamics of crystalline Ni based on molecular dynamics simulation using a well-established embedded atom potential, the Voter-Chen model.⁶ We focus on the (110) free surface since this interface is known to have a particularly high interfacial activity compared to other crystallographic interfaces, making this interface particularly important for applications.⁷ Our approach to characterizing the interfacial dynamics of crystalline Ni is unique in that it draws upon tools recently developed to characterize the collective dynamics of glass-forming (GF) liquids. We find below that these tools are highly suitable for characterizing the dynamics of these interfaces. It is expected that some atoms on the free surface will become “mobile” due to the “packing frustration” where the cooperative motion can be identified within these mobile particles. Due to packing frustration, the clusters of excessively *immobile* particles organize into dynamic structures of relative rigidity that coexist with strings of particles exhibiting cooperative motion, playing a role analogous to grain boundaries in polycrystalline materials.⁸ The glassy nature of the interfacial dynamics will then be characterized using van Hove correlation function, non-Gaussian parameter, and Debye-Waller factor. It is also expected that colored noise should naturally exist in the crystal interfacial dynamics since the existence of dynamic heterogeneity in the dynamics of condensed disordered materials means that there must be fluctuations in the self-diffusion coefficient, i.e., mobility fluctuations.^{9,10}

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: hao.zhang@ualberta.ca and jack.douglas@nist.gov

SIMULATION DETAILS

Molecular dynamics simulations were performed to characterize self-diffusion on Ni (110) free surface based on the same potential that we have utilized before for simulating Ni grain boundaries (GBs)⁸ and the interfacial dynamics and melting/freezing of Ni nanoparticles (NPs).^{11,12} In particular, atomic interactions for Ni were described using the Voter-Chen⁶ form of an Embedded Atom Method (EAM)¹³ potential. The simulation cell consists of $\approx 33\,000$ atoms with a dimension of about $7\text{ nm} \times 7\text{ nm} \times 7\text{ nm}$, oriented with crystallographic directions $[\bar{1}\bar{1}2]$, $[1\bar{1}0]$, and $[111]$ in the X-, Y-, and Z-directions. In all simulations, periodic boundary conditions were applied in X and Z-directions and free boundary condition was applied in Y-direction. Canonical ensemble (NVT) was employed and constant temperature (T) was maintained by the Nose-Hoover method.^{14,15} The MD simulations utilize LAMMPS,¹⁶ developed at Sandia National Laboratories.

In order to calculate the self-diffusivity D_s of interfacial atoms of the (110) interface of crystalline Ni, we heated our samples to fixed T values at which our isothermal simulations were performed: $T = 900\text{ K}$, 1000 K , 1100 K , 1200 K , 1300 K , 1400 K , 1500 K , 1550 K , and 1624 K . The “equilibrium melting temperature” T_m of 1624 K was determined previously for this potential using solid-liquid co-existence technique.¹⁷ At each T , simulations were conducted for at least 4 ns and in some cases extended to 10 ns . Self-diffusion coefficients D_s were determined from the slope of the mean-square-displacement $\langle r^2 \rangle$ of Ni atoms in the (110) interfacial layer versus time t . In particular, D_s is defined by $(1/N)\sum_{i=1}^N (\langle \Delta x_i^2 \rangle + \langle \Delta y_i^2 \rangle + \langle \Delta z_i^2 \rangle)/6t$ in the limit of long times where the sum ranges all the N atoms in the interfacial layer.

We define the interfacial layer in terms of the relative amplitude of atomic motion, the Debye-Waller factor (DWF), in this region in comparison to the DWF deep within the crystal. Specifically, we calculate the DWF as a function of depth away from the free surface and define the interfacial layer as the region near the crystal surface in which the DWF deviates appreciably from its average value deep within the crystal. At very low temperatures, this interfacial layer is an atomic monolayer, but as the temperature rises to about $1/2$ or $2/3$ the bulk crystal melting temperature T_m , this layer starts to extend over multiple layers. The atomic mobility, as defined by the Ni diffusion self-diffusion coefficient D_s in this “mobile” interfacial layer correspondingly rises more sharply than the simply Arrhenius behavior seen at lower temperatures. This super-Arrhenius interfacial dynamics in this temperature regime has long been recognized, but there has been no consensus about its origin. In our discussion below, we first quantify the super-Arrhenius relaxation above the onset temperature just mentioned and we also quantify the temperature dependence of the thickness of the “mobile” interfacial layer. Curiously, we find that the mobile interfacial thickness is directly related to the scale of collective atomic motion within this layer, just as found recently in glass-forming polymer films.¹⁸ As one might expect, the atomic mobility is substantially higher in this mobile layer than within the crystal. Since the interfacial atoms in that layer have more disordered configurations than the atoms within the crystal,

we could alternatively define interfacial widths in terms of equilibrium structural or energetic measures such as potential energy,¹⁹ structure factors,²⁰ radial distribution functions, and bond order parameter.²¹ However, previous simulation studies of metallic²² and polymeric glass-forming liquids¹⁸ have both demonstrated that such equilibrium properties *do not* strongly correlate with mobility gradients in the interfacial region of such films. On the other hand, the spatial variation of the Debye-Waller factor does seem to predict the spatial scale governing this type interfacial mobility gradient.²³ Since we are interested in atomic mobility within the interfacial layer of crystals, we define the interfacial layer thickness in terms of a suitable mobility measure, the Debye-Waller factor.

RESULTS AND DISCUSSION

There have been numerous observations for both crystalline and GF materials,^{5,24–27} indicating that the interfacial mobility can be orders of magnitude larger than the bulk material, a phenomenon having profound implications for many applications. As noted above, it has often been noticed that the temperature dependence of the surface self-diffusion coefficient D_s of crystalline materials exhibits non-Arrhenius temperature (T) dependence, prompting much speculation about the possible role of collective atomic motion to explain this phenomenon.^{28–30} Given our approach to describe the interfacial dynamics of crystals, this seems to be a good starting point for our investigation of the interfacial dynamics of crystals.

The inset of Fig. 1 shows representative surface diffusion coefficient D_s data for Ni (110) and Cu (110) free surfaces as a function of T where we have introduced reduced units for both T and D_s , where D_s is normalized by its value D_{so} at the melting temperature, T_m . The often-quoted non-Arrhenius temperature dependence of D_s is apparent in this plot (see Fig. 3 of Ref. 31), and we next consider whether our molecular dynamics simulations of Ni can reproduce this effect. In general, the “interfacial region” of the crystal is a layer of enhanced mobility rather than just an atomic monolayer and the average thickness of this layer ξ varies with temperature, as we quantify below. The data in Fig. 1 denote D_s in the entire interfacial layer.

To ensure the robustness of our results to the choice of interatomic potential, we calculate D_s of Ni on the (110) interface region based on both the Voter-Chen model⁶ and the more recently introduced ReaxFF potential.³⁴ In addition to observing a non-Arrhenius temperature dependence for D_s that is similar to the experimental trend, we find that our estimates for the reduced interfacial D_s , i.e., D_s/D_{so} , are essentially independent of the choice of potential. This agreement holds despite the fact that T_m estimates for EAM potentials normally vary by as much as 100 K from experimentally observed values. In the particular case of Ni, for example, a recent survey of EAM estimates of T_m range from 1478 K to 1890 K , while the experimental value is $T_m = 1728\text{ K}$.³⁵ For the particular EAM potentials considered in Fig. 1, we have $T_m = 1624\text{ K}$ for the Voter-Chen model and $T_m = 1724\text{ K}$ for the ReaxFF potential. The ReaxFF potential evidently agrees

FIG. 1. Molecular dynamics simulation of the surface diffusivity D_s of Ni on the (110) interface as a function of reduced temperature, T_m/T . The inset shows experimental results of reduced surface diffusivity in Ni (110) and Cu (110) as a function of reduced temperature.^{30,31} Previous compilations of D_s data for many metals indicate the dependence of $D_s/D_s(T_m)$ on T/T_m is nearly universal for a range of common metals (Fe, Au, Ni, Cu, and Ag).^{32,33}

better with the experimental T_m . We conclude that we have greater transferability of the results from one simulation model to another, and with experiment, if we report in terms of reduced temperature units, a simple procedure first introduced in an experimental context by Gjostein.³³ Below, we limit our simulations to the Voter-Chen model and we report our observations in suitably defined reduced variables.

What is the origin of the non-Arrhenius temperature dependence in the interfacial mobility of crystals? We see that the experimental trend has a different character than D_s in glass-forming liquids since the non-Arrhenius scaling of D_s develops upon *heating* rather than cooling in the crystal interfacial mobility. Nonetheless, there have been a number of previous studies suggesting that some sort of collective atomic motion^{7,29,36} underlies this non-Arrhenius dynamics, as suggested by the Adam-Gibbs model in the context of

the dynamics of glass formation and evidenced by many computational and experimental observations indicating direct evidence for concerted atomic motion on the interfaces of crystals.^{37–41} A generally accepted model of how the collective motion relates to the activation energy governing transport has not yet been established, however. We next examine the extent to which the interfacial dynamics of Ni resembles the dynamics of a glass-forming liquids based on theoretical tools familiar from the field of cooled liquids rather than heated crystals.

In Figure 2, we examine the temperature dependence of the mean square atomic displacement ($\langle r^2 \rangle$) of interfacial atoms in the (110) surface as a function of time t over a temperature range from 900 K to 1550 K (or from $0.55 T_m$ to $0.95 T_m$). At short times, we see ballistic motion associated with particle inertia, while at long times, we observe a caging. The caging

FIG. 2. Mean squared atomic displacement ($\langle r^2 \rangle$) of interfacial atoms in the (110) boundary of Ni as a function of time over a range of temperatures between 900 K and 1550 K ($0.55 T_m$ – $0.95 T_m$). The Debye-Waller factor $\langle u^2 \rangle^{1/2}$, reduced by the mean interparticle distance σ , is shown as an inset. The amplitude of the interfacial atoms is much larger than for those within the crystal, as we shall discuss below.

becomes weaker, shorter lived and D_s increases upon heating, similar to almost any cooled liquid. The Debye-Waller factor $\langle u^2 \rangle$ is defined by $\langle r^2 \rangle$ at a picosecond caging time and this experimentally measure of the scale of particle localization, reduced by the interparticle distance parameter σ , is shown in inset to Fig. 2. As the melting temperature is approached, the mean square particle displacement increases sharply,²⁸ signaling the onset of particle delocalization. Thus, there is nothing surprising about the interfacial diffusion data in relation to former observations on crystal melting and cooled liquids. A closer look at the interfacial transport reveals a more complex situation, however.

In Figure 3, we examine a well-known measure of mobility fluctuations taken from the field of glass-forming liquids, the non-Gaussian parameter, α_2 . This quantity has a simple definition in terms of moments of the particle displacement distance from their initial position at $t = 0$ after time Δt ,

$$\alpha_2 \equiv (3\langle r^4(\Delta t) \rangle / 5\langle r^2(\Delta t) \rangle^2) - 1. \quad (1)$$

The non-Gaussian parameter α_2 is defined to equal zero for Brownian motion and this measure of dynamical heterogeneity (DH) has often been considered in previous MD simulation studies of GF liquids,⁴³ GBs,⁸ and the interfacial dynamics of NPs.¹¹ We see that the peak value of α_2 grows as we approach the melting temperature, signaling heterogeneous dynamics. The $\alpha_2(t)$ peaks at a characteristic diffusion timescale⁴² t^* and the inset of Fig. 3 shows that D_s/T scales in inverse proportion to t^* , confirming in the context of the interfacial dynamics of crystals a relation established before in glass-forming liquids.⁴² This scaling relation has also been observed in the homogeneous melting of crystalline Ni, yet another material exhibiting dynamic heterogeneity.⁴⁴

We next focus on the particular form of collective motion occurring in the interfacial dynamics of crystalline Ni using computational tools drawn from the field of glass-forming liquids. The van Hove correlation function $G_s(r, t)$ describes the distribution function for particle displacements from an

arbitrary origin at $t = 0$ to a distance $r(t)$ at time t and our illustration of this quantity in Fig. 4 shows a multi-peaked structure characteristic of particle hopping, symptomatic of the presence of relatively stationary atoms and those moving quickly to positions that are multiples of the interparticle distance.

We can define *mobile particles* as those that make displacements beyond the first minimum in $G_s(r, t)$ at the characteristic diffusive time, t^* . This well-defined cutoff scale is about 1.5 Å in Fig. 4 and only varies weakly with temperature. An examination of the mobile particles shows that their positions are highly correlated in space in the form fractal structures whose size increases upon heating rather than upon cooling as in GF liquids, so we are seeing something similar to our normal experience with GF liquids and grain boundaries. In a series of recent papers, we have investigated collective motion in GF liquids, as well as in Ni GBs and in the interfacial dynamics of Ni NPs, and in each case, there is a similar development of clusters of mobile clusters upon changing temperature. The lifetime of these dynamic clusters is governed by the mass diffusion relaxation time, t^* .⁴²

Investigations of other strongly interacting particle systems have consistently led to the conclusion that these clusters of mobile particles are themselves clusters of more primitive clusters of atoms undergoing string-like correlated motion so that the *mobile particles clusters* are composed of sub-elements undergoing cooperative motion. An examination of the specific geometrical form of the collective motions occurring on the (110) surface of crystalline Ni reveals that we are dealing in some sense with essentially the *same physical phenomenon*, cooperative string-like collective motion. We have repeatedly described our method for determining these dynamic structures in recent publications in other physical contexts and thus, we describe our method of characterizing this motion in supplementary material.¹¹⁴ The basic idea is that we sort the mobile particles into clusters that stay within about an interparticle distance from each other within the lifetime over which the mobile clusters and strings exist, i.e., t^* .

FIG. 3. The non-Gaussian parameter α_2 as a function of time over a range of T over which non-Arrhenius diffusion is observed in the interfacial dynamics. The time t^* at which α_2 peaks value defines a diffusive characteristic time and we show in the inset D_s/T versus of t^* to emphasize this relation. α_2 is normally taken to be a measure of dynamic heterogeneity in cooled liquids and its increasing value upon heating here signals the presence of large mobility fluctuations⁴² in interfacial dynamics of crystals that grow as the melting temperature is approached. An examination of the intermediate scattering function indicates a non-exponential stretched exponential decay with stretching exponent β similar to our previous observations on the dynamics of Ni grain boundaries,⁸ pointing further to the similarity of the interfacial dynamics of crystals to GF liquids.

FIG. 4. van Hove self-correlation $G_s(r, t)$ describing the displacement of Ni interfacial atoms on the (110) interface upon approaching the melting temperature. Note the tendency of the interfacial atoms to hop preferentially to multiples of the average interparticle distance, $\sigma \approx 2.5 \text{ \AA}$.

Figure 5 illustrates representative string excitations within the interfacial region of the (110) interface of Ni. There is indeed a tendency for string-like coordinated particle displacements as suggested long ago by Rhead,²⁸ Binh and Melinon²⁹ and Bonzel and Latta.³⁰ We see in Fig. 5 that the strings are distributed rather uniformly in the direction transverse to crystal interface, but their in-plane distribution is rather “spotty”. It is evident that the pre-melted state of heated crystal interface is neither like a crystal nor a simple liquid, but this mobile interfacial layer is rather more like a glass-forming liquid, both in terms of its dynamical motions and average geometrical structure. We expect this to be a rather universal phenomenon in crystalline materials with many implications for materials science broadly.

There are rather practical reasons for being interested in the strings. In the context of GF liquids, the string length, along with high temperature Arrhenius parameters, allows

for the quantitative prediction of relaxation times and diffusion in GF liquids.^{23,49–52} It would be evidently interesting to establish whether this type of quantitative relation between the string length and D exists for the interfacial dynamics of crystals where the natural reference state of the crystal is the low temperature crystal state rather than a high temperature fluid.

Following previous work on glass-forming polymeric liquids in the form of bulk materials, polymer nanocomposites, and thin polymer films,^{18,49} metallic glass materials such as Ni₈₀P₂₀ modeled by simple Lennard-Jones potentials^{42,43,53} and our former treatments of grain boundaries⁸ and Ni NPs,¹¹ we quantify the average length L of the strings illustrated in Fig. 5 by first calculating their distribution. As we have always observed before in characterizing string-like motion, the string length distribution shown in Fig. 6 is nearly exponential, characteristic of an equilibrium polymerization process, a

FIG. 5. Profile and side views of the interfacial region of the (110) interface of crystalline Ni at $T/T_m = 0.92$. The measurements of Cao and Conrad⁴⁵ indicate that the (110) interface of Ni begins to broaden near $\approx 0.5T_m$. The interfacial width becomes significant around $\approx 0.75T_m$, which is T range in which the non-Arrhenius variation of D_s becomes conspicuous in Fig. 1. A similar break point in D versus reduced T has been observed in the interfacial mobility data of numerous metals (Cu, Nb, Ni, Mo, Rh, Pt, W, Ta).^{29,46} The onset of interfacial mobility can be expected to correspond to the onset of the reactivity in solid materials and, indeed, Tammann’s empirical rule for solid state reactivity indicates that solid materials generally become reactive for $T \approx (1/2 \text{ to } 2/3)T_m$.^{47,48} Recent simulations examining the interfacial dynamics of GF polymer liquids indicate that these materials also have a mobile particle interfacial layer whose thickness is determined by the average string length,¹⁸ L . We consider such a relation for the Ni (110) interface region in Fig. 7 where we see a similar correlation as found in polymer GF films.

FIG. 6. Length distribution of strings in the interfacial region of (110) Ni over a range of T . Inset shows a direct comparison of the string length and change in the relative value of the apparent activation energy for diffusion, $Q(T)/Q$ (bulk crystal).⁵⁴

particular kind of self-assembly.⁵¹ We emphasize that while strings as long as 10 atoms are evident in our simulations, the occurrence of such long strings is not common so that the *average* string length L is much smaller; the corresponding average string length L as a function of T is indicated in the inset. Our uncertainty estimate is based on a 95% confidence interval and does not account for systematic errors associated with the lack of full equilibration. In GF liquids, the string length L determines the change of activation free energy for both structural relaxation and diffusion and in the inset, we compare L to the change in the apparent activation free energy associated with the interfacial diffusion coefficient of Ni within its (110) interfacial region. We find that the average string length *quantitatively* describes the change of the activation energy for transport for the pre-melted state¹⁰ of Ni. Bonzel³¹ has developed a generalized transition state theory predicting that the average barrier height for crystal interfacial atoms diffusion at high temperature should increase with the average number of atoms participating in these collective barrier crossing events, a prediction that is fully in accord with our observations. The apparent activation energy for diffusion $Q(T)$ was determined by the slope at each temperature in Figure 1. We emphasize that the average string length L in the interfacial region grows upon heating the crystal, while in GF liquids, it grows upon cooling so that the present work is a non-trivial extension of former findings on GF liquids.⁵⁰

Recent simulations on interfacial dynamics of GF polymer films have indicated that the thickness of the high interfacial mobility layer at the “free” film interface exhibits a linear variation with L in these films.³³ This finding has been further confirmed by Shavit and Riggleman⁵⁵ who found this relation holds both under equilibrium and aging conditions where the interfacial length and L together evolve in time. In separate work on the same polymer material in bulk, Shavit *et al.*⁵² show that the evolving structural relaxation time under aging conditions correspondingly grows in a way that can be predicted to a good approximation by the growth of $L(t)$. Freed^{51,56} has developed a generalized transition state theory for the dy-

namics of glass-forming liquids that parallels the earlier calculations of Bonzel. These theories lead to a common conclusion that the free energy of activation is proportional to the average number of particles involved in the collective barrier crossing events.

It is interesting to consider whether a similar relation L and atomic mobility holds for our crystalline material, which likewise exhibits a “pre-melting” transition into a state that is similar in many ways morphologically to a GF liquid. In Fig. 7(b), we directly plot our estimate of the thickness of the interfacial layer of the (110) interface of Ni against our independent estimate of L given above. We see that these quantities indeed track each other rather well. A better way to estimate the thickness of the mobile interfacial layer of the crystal would be to estimate the dynamic structure factor and structural relaxation time layer by layer from the collective intermediate scattering function, as in the treatment of Hanakata *et al.* for GF polymer films.¹⁸ The present brief treatment of the thickness of the mobile interfacial layer indicates that its thickness ξ (determined between the point where the Debye-Waller factor starts to deviate from the bulk value and the point corresponding to the maximum value, as indicated in Fig. 7(a)) is directly related to the scale of collective motion within the interfacial layer L , just as found in former studies of the interfacial dynamics of NPs¹⁰ and GF polymer films.³³

Mean field treatments of “pre-melting”^{57,58} have predicted the formation of a liquid layer on the crystal interface whose thickness depends on the free energy difference between bulk liquid and solid phase, solid-liquid interfacial energy, liquid surface tension, and long-range dispersion interactions. With the presence of only a short-range interatomic force, the model predicts that a logarithmic divergence of this liquid layer thickness with increasing temperature toward T_m .⁵⁹ However, it is not clear to us how this thermodynamic model relates to our observations since the mobile interfacial layer does not obviously correspond to a “liquid” thermodynamic state.¹⁰ It is possible for a crystal to sustain high atomic mobility, so

FIG. 7. (a) Top left. Variation of Debye-Waller factor along Y-axis and the corresponding atomic configuration (atoms are colored by potential energy) at $T = 1000$ K. The thickness of the mobile surface layer is determined between the point where the Debye-Waller factor starts to deviate from the bulk value and the point corresponding to the maximum value. The DWF profile along Y-axis can be well fitted by an exponential function (blue solid line), as found in recent experimental studies on colloidal crystals.⁶⁰ Bottom left. Snapshot of atomic configuration with scales determined from the top figure indicated. (b) Comparison of the thickness of the “surface melted layer” and the scale of collective motion in the (110) interface of Ni as a function of reduced temperature, T/T_m .

atomic mobility by itself does not define the liquid state.⁴⁴ In our previous study of the structural ordering of the interfacial layer of “pre-melted” surfaces of Ni NPs, we found these interfaces to exhibit a substantial degree of local ordering so that these layers might reasonably be characterized as “crystalline” from a structural standpoint.¹⁰ Evidently, the pre-melted state cannot be neatly categorized as being a simple liquid or solid, but rather seems to be in a material condition somewhere in between these ideal states of matter. At any rate, it is evident from Fig. 7(b) that the thickness of the mobile interfacial layer does not seem to diverge as T approaches the bulk melting temperature T_m as one would expect from the mean field theory of pre-melting. It is possible that the approach to equilibrium becomes very slow near T_m , leading to a systematic error in both our D_s and L estimates near this phase transition. The temperature range near T_m will require a closer examination in future work to see if this discrepancy between our simulation estimates of the mobile interfacial thickness and the “liquid” layer thickness of the pre-melting model near T_m can be understood as in the aging studies of Shavit *et al.*^{52,55} in the context of film and bulk glass-forming polymer materials.

Quite apart from our observations of collective motion influencing the rate of diffusion and relaxation in the interfacial dynamics of crystals, there are other implications of these interfacial excitations for the properties of condensed materials and for manufacturing and measurement applications. It is well known that metallic films are typically “noisy”, exhibiting anomalous colored noise with power law exponent α in the power spectrum describing fluctuations in various properties (particle mobility, potential energy, etc.) that is dependent on T . This noise is arguably a fundamentally limiting factor in diverse manufacturing applications involving the development of electrical devices⁶¹ and sensors,⁶² and this type of thermal noise is often found as a complication to high resolution measurement and sensing processes. While it has long been appreciated that this ubiquitous “ $1/f$ ” noise is an equilib-

rium, or near equilibrium, phenomenon in many condensed materials having an origin in mobility fluctuations, a general explanation of this phenomenon has remained elusive. Recently, in our investigation of the interfacial dynamics of Ni nanoparticles,^{9,10} we have found that the exponent α describing intermittent displacement fluctuations related to mobility fluctuations can be directly related to the average string length L under a wide range of conditions (doping the surface with different atoms to tune the scale of collective motion up or down depending on the type of interfacial additives, varying nanoparticle size, etc.). In particular, it was found that L was directly related⁹ to α for particle displacement fluctuations ($\langle u^2 \rangle$). Specifically, we find $\alpha \approx L - 1$. This relation is interesting for several reasons. First, it allows for the determination of the scale of collective motion L from noise measurements, providing access to a quantity that is otherwise difficult to determine experimentally, apart from the direct particle tracking methods described in the present work. While this is possible for colloidal particles,^{63,64} this direct method of estimating L is certainly not normally possible for atoms and molecules. This interrelation between noise color (α) and L is also interesting since recent developments in the area of GF liquids give insight into the physical factors that govern the temperature dependence of collective motion (as quantified by L), both from analytic and simulation perspectives, and thus, we are in a position to *engineer* the color of the noise (i.e., the value of α) for applications. Often this means in practice making the “blinking” phenomenon^{65–67} in the property measurement of interest “go away”⁶⁸ so that the noise does not interfere with device function or measurement, but we can image more subtle use of this noise modulation in sensing,^{69–72} emulating the sensory receptive behavior of biological systems.^{73–75}

We next examine the extent to which our former results relating colored noise and the extent of collective motion in the interfacial dynamics of Ni NPs extends to the interfaces

of macroscopic crystals. This extension is not obvious since the interfacial dynamics of Ni NPs¹¹ and Ni GBs⁸ are more like the dynamics of glass-forming liquids than the interfacial dynamics of the (110) interface of Ni crystals. In both GBs and NPs, the scale of collective motion grows upon cooling, while scale of collective motion is somehow growing in the interfacial dynamics described above. This originally surprised us until we realized that the strong interaction between the different crystallographic faces of NPs tends to create frustration in the NP dynamics similar to the competition between different grains in GB dynamics. This frustration simply does not exist when the crystal becomes macroscopic so that the different crystallographic interfaces effectively decouple from each other. (The NP size at which this decoupling emerges has not yet been established.) As a consequence, we have found that the atomic mobilities on each of the crystallographic interfaces of Ni are strikingly different, both in terms of the scale of collective motion and in their magnitude of interfacial mobility at temperatures well below T_m (see Discussion). This

is a complex topic requiring a separate publication and we next focus on examining whether we can observe a quantitative relation between the scale of collective motion and colored noise governing mobility and potential energy fluctuations in the case of the (110) interface of crystalline Ni.

Potential energy fluctuations of the interfacial atoms are perhaps the simplest property to consider computationally. In Fig. 8(a), we consider a time series of the potential energy fluctuations of the mobile interfacial atoms in the interfacial region of (110) Ni. There seems to be some evidence in this figure for *two-level fluctuations*, as observed before for simulations of the interfacial dynamics of Ni NPs.¹⁰ To quantify and contrast this phenomenon with the dynamics of “normal” or non-mobile Ni atoms, Figure 8(b) compares potential energy fluctuations of atoms that are involved in collective string-like motion (blue), extended to timescale longer than the lifetime of the strings atoms, to the potential energy fluctuations of particles that are not in this excited *mobile particle state*, red and green curves indicate results for interfacial and bulk

FIG. 8. (a) Potential energy fluctuation of individual mobile atoms on the (110) surface of Ni at 1100 K. We show the energy fluctuation of 12 mobile atoms where the energy scale has been shifted for clarity. (b) Comparison of potential energy fluctuations of atoms that are involved in collective string-like motion (blue) to potential energy fluctuations of particles that are not in this excited mobile particle state, the red and green curves indicate results for interfacial and bulk atoms of this type. The inset shows the energy distribution of the interfacial string atom where we show that these particles are transitioning between two well-defined bands of energy states. In contrast, the non-mobile interfacial atoms exhibit a similar large variance in their energy fluctuations, but these fluctuations lack a two-level system character. (c) Quake-like fluctuations in u^2 of atoms involved in collective string-like motion. The large jumps coincide with the energy jumps in Fig. 8(a). (d) Probability distribution function $P(u^2)$ for the singular avalanche events for the u^2 where we observe a power law scaling, $P(u^2) \sim (u^2)^{-\gamma}$. The inset shows how varying temperature affects this quake phenomenon. We find that γ varies approximately linearly with $1/T$.

non-mobile Ni atoms. We see that the potential energy fluctuations of the interfacial atoms have a much larger variance than the bulk atoms, but the inset shows mobile interfacial atoms involved in string motion are transitioning between two well-defined bands of potential energy states, as evidenced by the *bimodal* distribution in their potential energy. The fluctuations in the atomic positions of the interfacial atoms, as measured by $\langle u^2 \rangle$, are likewise much larger than those for the bulk atoms (see Fig. 2) where interfacial $\langle u^2 \rangle$ values are typically about twice as large as bulk values at the same T . This is not surprising, but we see that the jumps in potential energy in Fig. 8(a) are correspondingly accompanied by jumps in magnitude of u^2 . Figure 8(c) illustrates a time series of u^2 values obtained by the interfacial string atoms. These singular particle displacement events are reminiscent of avalanches seen in diverse amorphous materials and this “quake” phenomenon is discussed extensively in our previous work.¹⁰ To quantify this phenomenon in the context of macroscopic crystal interfacial dynamics, we show the probability distribution function $P(u^2)$ of the peak values of (u^2) in Fig. 8(d), the magnitude of these avalanche displacement events. As in our former NP study,¹⁰ we find a Richter-like scaling, $P(u^2) \sim (u^2)^{-\gamma}$. The inset shows that the quake exponent γ varies nearly linearly with $1/T$, reflecting the growing scale of collective motion L upon cooling, an effect quantified below.

It is visually apparent that the energy fluctuations in Fig. 8(a) exhibit long range correlations so that we examine the power spectrum of this type of time series data following the same procedure of our past work on Ni NPs⁹ to quantify the nature of these fluctuations. We also applied this procedure to the time series for displacement fluctuations ($\langle u^2 \rangle$) to compare these with the energy fluctuation data and we show the result of this power spectrum analysis in Fig. 9. In this figure, we find the fluctuations of *all* the interfacial atoms to be entirely consistent with our former work on the interfacial dynamics of Ni NPs. Not only do the power law exponents governing noise fluctuations in the potential energy and local caging (mobility) exhibit the same trend with T , but the noise exponents for the potential energy and $\langle u^2 \rangle$ fluctuations are also identical within numerical uncertainty at all T , a relation

that did not hold in NPs. Previously, we suggested that this relation might be true for bulk materials, but we did not expect this relation to apply to the interfacial dynamics of crystalline materials because we thought interfacial roughening would lead to colored noise in the energy fluctuations distinct from the displacement fluctuations. This common variation of the noise exponents is thus surprising to us. Here, we also observe that the quake exponent γ varies inversely to the colored noise exponent so that the noise “color” is directly related to the quake intensity distribution. This finding is not yet understood, but we have a clue into the origin of the displacement intensity fluctuations.

We next consider the extent to which the noise exponents are related to the extent of collective motion to consider the possible use of these noise exponents to inform on the scale of collective motion in the interfacial dynamics of crystals. In our previous work, we found the exponent relating to $\langle u^2 \rangle$ was related to the average value of L by a simple linear relation so that more correlated noise translates into a corresponding more extended collective motion. In Figure 10, we examine this relationship in the context of the (110) interfacial dynamics of Ni. We see that while L and α vary in a roughly linear fashion over the range in which we can obtain reliable estimates of the noise exponents, the precise relation $\alpha = L - 1$ does not precisely describe the interfacial dynamics of the (110) interface of crystalline Ni. Still, we may conclude that the “color” of the E and $\langle u^2 \rangle$ noise fluctuation exponents are somewhat correlated with the extent of collective motion, L . The results of Fig. 9 then imply that “quake exponent” γ is roughly correlated with the scale of collective motion, L .

Finally, we consider the role of impurities on the character of collective motion in the interfacial dynamics of our Ni interfacial dynamics. Real surfaces are normally accompanied by the presence of impurities whose presence can profoundly influence the interfacial dynamics of crystalline materials. In previous work,¹¹ we showed how the presence of Ag, Au, and Pt atoms altered the interfacial dynamics of Ni NPs through the modification of the scale of collective motion by these additives. In the catalytic processes involving Ni and in relation to the Ni polycrystalline materials, S is heavily implicated as

FIG. 9. Power spectrum exponent for potential energy (left figure) and $\langle u^2 \rangle$ fluctuations (right figure) of mobile particles within the (110) interface of Ni over a range of T below T_m .

FIG. 10. Comparison between power spectrum exponent for potential energy and the average string length L where α exponent estimates near T_m are excluded because they seem to diverge near T_m , making their estimation highly uncertain.

an impurity that can cause great changes in crystal interfacial mobility and it is natural to explore how phenomenon in the context of the interfacial dynamics of the (110) interface of Ni. As in our former work on metal impurities in Ni NPs, we find that adding a small amount of S has the effect of modulating the scale of collective motion and the GB diffusion coefficient of Ni, an effect illustrated in Figs. 11 and 12.

In Figure 11, we observe that adding a relatively small amount of S has the effect of appreciably reducing the Ni mobility at $T/T_m = 0.81$ (Figure 11), an effect actually observed experimentally in the interfacial dynamics of the (110) interface of Ni⁷⁶ and understandable from how S alters the scale of collective motion of the Ni atoms within the Ni crystal (110) (see Fig. 12). In particular, by adding $\approx 10\%$ S atoms onto the Ni (110) surface at $T/T_m = 0.81$, the self-diffusivity of the Ni atoms becomes reduced by more than a factor of 2, while the average string length increases by $\approx 20\%$. The observed

trend suggests a very abrupt reduction of mobility when the concentration is about the percolation value of 15% S atoms. The impurity (S) atoms seem to be confined to the interfacial mobility layer of thickness ξ discussed above so that the impurities are localized to the interfacial layer of the crystal, an effect that should be studied more thoroughly for other impurities and interfaces.

The reduction of the interfacial mobility of Ni with the addition of S is surprising given the well-known embrittlement of Ni materials⁷⁷ due to the presence of S impurities in the grain boundaries of polycrystalline Ni, an effect suggesting that in this situation, S might be greatly *increasing* the GB interfacial mobility, thus compromising the structural integrity of Ni polycrystalline materials. To better understand the trend in Figs. 11 and 12, we also investigated the addition of S to the Ni GBs and to the interfacial region of Ni NPs through an extension of our former modeling of the interfacial dynamics

FIG. 11. Change in the surface diffusion coefficient of Ni in the interfacial region through the addition of a small amount S at the reduced temperature, $T/T_m = 0.81$.

FIG. 12. Change of the scale of collective atomic motion in the interfacial region of the (110) interface of Ni through the addition of S at the reduced temperature $T/T_m = 0.81$.

of Ni NPs to include this type of “impurity”. In the case of Ni NPs, the S additive indeed greatly enhances rather than diminishes the interfacial mobility of the Ni atoms in the GB region so that the critical force required for catastrophic slipping of the Ni GBs drops sharply with an increasing S concentration. Evidently, the impact of impurity on the crystal dynamics greatly depends strongly on the type of interface to which they are added.

We conclude that surface impurities can greatly alter the interfacial mobility of crystal interfaces through the modulation of the scale of collective motion, leading sometimes to increases and sometimes to decreases of the interfacial mobility.⁷⁸ The general principles underlying these large impurity induced mobility changes in these different types of interfaces remain to be investigated fundamentally, however. This sensitivity of interfacial dynamics to impurities and interface type of interface offers a powerful handle for engineering materials and for controlling catalytic growth processes and syntheses exploiting the collective dynamics of metal interfaces.

CONCLUSIONS

We have investigated the collective atomic dynamics of interfacial region of crystalline Ni and have focused in our initial study on the most mobile interface, the (110) interface, where highly anharmonic interatomic interactions are known to be prevalent.^{7,36,79} The interfacial dynamics of this material is characterized by well-defined string-like collective excitations similar in geometry and significance in relation to transport properties to the string excitations observed in glass-forming liquids,^{18,49,42,43,53} i.e., the average string length is found to correlate with the change in the activation energy for diffusion. Generalizations of transition state theory to describe barrier crossing events involving collective atomic motion in both the interfacial dynamics of crystals³¹ and glass-forming liquids^{51,56} are entirely consistent with this correlation

between string-length and the activation energy for transport. We have further shown that the presence of these collective excitations is related to colored noise in potential energy and particle displacement fluctuations, thus providing a means to estimate the scale of collective motion L and quake intensity exponent γ and a strategy for controlling “flicker” noise in diverse applications where this type of thermal noise limits measurement or signal resolution. The finding of fundamental defect structures underlying the occurrence of colored noise in crystalline materials is also a finding having practical and theoretical significance. Finally, we show that the addition of impurities to the interfacial region of a crystalline material provides a versatile method for tuning the dynamics of interfaces to achieve manufacturing goals such as optimal catalytic efficiency and control of the unique form of synthesized product. Selectively capping the different crystal interfaces with peptides and surfactants provides a versatile method to engineer nanoparticle shape.^{80–82} A deeper understanding of the interfacial dynamics of crystalline and non-crystalline materials has many potential applications in materials design and improved material performance.

The relatively high interfacial mobility of ice in geophysical and atmospheric contexts is another area where our approach to characterizing interfacial mobility may prove valuable. The slipperiness of ice, frost heave, and catalytic properties of ice crystals in the atmosphere, along with diverse other phenomena are greatly influenced by the “surface melted” interfacial layer of ice.^{24,83,84}

As a final point, we emphasize that the (110) surface is but one type of interface type for crystalline Ni; each interface type seems to have its own distinct character in terms of both structure and dynamics. An investigation of the many issues involved in these other interfacial types is beyond the scope of the present work, but we briefly note that a high level of kinetic anisotropy can exist on the different crystallographic interfaces at high undercooling values that are well below T_m .^{85,86} This high kinetic anisotropy is natural when

FIG. 13. The Debye-Waller factor $\langle u^2 \rangle^{1/2}$ reduced by the mean interparticle distance σ for the loose-packed (110) interface and the close-packed (100) and (111) interfaces. The amplitude of motion on the loose-packed interface is clearly much larger than for the close-packed interfaces, a phenomenon having large practical implications for crystal growth and the interfacial dynamics of crystals. We can estimate for the onset of relatively high interfacial mobility from the peak of the van Hove correlation function and the ratio $\langle u^2 \rangle^{1/2}/\sigma$. In particular, “surface pre-melting” corresponds well to the condition $\langle u^2 \rangle^{1/2}/\sigma \approx 0.25 \pm 0.03$, a value consistent with our former estimate of critical melting in bulk Ni^{44,67} and with experimental estimates on colloidal fluids by Alsayed *et al.*⁶⁰ We suggest that this condition determines the onset condition for substantial interfacial mobility for each interface, and the dotted red line in Fig. 13 shows our estimate of the Tammann temperature implied for the different interfaces that we have simulated based on an interfacial Lindemann criterion (see text).

one considers that the different crystal interfaces exhibit rather different packing characteristics, which greatly influence the non-Arrhenius dynamics on each crystallographic interface.⁸⁷ Recent work by Binder and coworkers⁸⁸ has suggested that the interfacial mobility of crystals has a large impact on the growth rate and melting rate of crystals under far from equilibrium conditions.

The anisotropy in packing on the different crystallographic interfaces and its influence on the fast (i.e., pico-second) interfacial dynamics can be quantified by comparing the magnitude of the Debye-Waller factor $\langle u^2 \rangle$ of the interfacial atoms on the different crystallographic interfaces. Figure 13 compares $\langle u^2 \rangle^{1/2}$, reduced by the mean interparticle distance $\sigma = \langle \sigma^2 \rangle^{1/2}$, as a function of T for the “loose-packed” (110) versus the close-packed (100) and (111) crystal interfaces where we see a large disparity in the relative average amplitude of local vibrational motion. The large disparity between the

magnitude of $\langle u^2 \rangle$ for interfacial atoms, and between atoms on different crystal interfaces, has been observed in numerous surface scattering studies.^{89–92}

In Fig. 14, we directly examine the interfacial mobility (D_s) of Ni atoms for representative close and loose packed crystallographic interfaces of Ni, where we only consider temperatures larger than the glass transition temperature T_g , corresponding to a reduced temperature T/T_m between 3/2 and 2.^{93–98} (Notably, the same condition seems to define the Tammann temperature governing the onset of interfacial mobility in crystalline materials.^{41,42}) We see that the interfacial mobility on the different crystallographic interfaces can differ by *orders of magnitude*, loose-packed interfaces such as (110) and (103) interfaces exhibiting a much higher mobility than the close-packed (111) and (100) interfaces. Each interface exhibits a separate “crossover temperature” above which the D_s becomes non-Arrhenius and this crossover temperature

FIG. 14. Comparison of the surface diffusion coefficient for various types of crystallographic interfaces as calculated from the Voter-Chen model. The data denoted “bulk” (pink triangles) correspond to a simulation with no free boundaries where appreciable superheating occurs.⁴⁴ Note the tendency of these curves to intersect at common point, which means that changes in the activation energy are correlated with changes in the prefactor.^{7,79,103–105} This entropy-enthalpy compensation effect, and the associated large variation of the diffusion prefactor, has frequently been reported in recent measurements of epitaxial crystallization and surface diffusion,^{2,106} diffusion in alloys,¹⁰⁷ and in simulations and experiments of grain boundary mobility.¹⁰⁸ Entropy-enthalpy compensation has also been seen in simulations of interlayer diffusion on the interfacial region of the (110) interface of Cu.⁷

can be estimated from a particle delocalization or surface pre-melting criterion, $\langle u^2 \rangle^{1/2}/\sigma \approx 0.25$, applied to the interfacial atoms (see Fig. 13). While there is no evidence that this transition in the interfacial dynamics can be identified with any kind of phase transition in the T range we study, there is clearly a dynamical transition in the character of the interfacial atomic motion when the amplitude of the local vibrational motion becomes sufficiently large relative to the average interparticle distance. Thus, we have a Lindemann-like condition^{60,99} for the onset of interfacial mobility in crystals that is distinct from the usual condition of bulk melting.

One can also directly visualize this kinetic mobility anisotropy in a qualitative way by observing the shapes of the crystals using a scanning tunneling microscope (STM) where we see that loose-packed interfaces become rounded above the cross-over temperature $T/T_m > 0.75$, while the close-packed interfaces remain faceted well above this temperature range.^{87,100,101} Since packing efficiency is heavily implicated as a factor regulating the scale of collective motion in cooled liquids,¹⁰² we can also expect a considerable variation in the character of the collective motion on the different interfaces from the (110) interface. A quick check of Ni self-diffusion on the (111) interface reveals the presence of highly collective motion in the form of strings, as in the case of the (110) interface, but L for the (111) interface exhibits virtually *no temperature variation*, explaining the approximately Arrhenius temperature dependence of D_s on this interface over a large temperature range (see Fig. 14). We emphasize, however, that collective motion does not by itself imply a non-Arrhenius relaxation and we have seen the same behavior in glass-forming liquids where residual collective motion can exist even at high temperatures where relaxation becomes Arrhenius.⁴⁴ We also see in Fig. 14 the “odd” result that the reduced diffusion coefficient $D_s/D_s(T_m)$ on the (111) interface can be orders of magnitude smaller than 1 for T near T_m . However, this behavior is understandable when we realize that this interface is observed experimentally to *superheat* (see Fig. 13).¹⁰¹ We plan to discuss properties discussed in the present paper for the other crystallographic interfaces in a separate paper. Finally, we speculate on some practical ramifications of a large kinetic anisotropy on the nature of far from equilibrium crystal growth.

A strong kinetic anisotropy¹⁰⁹ along different crystallographic interfaces and correlated motion and fluctuations at the growth front^{12,109–111} can be naturally expected to lead to a strong tendency towards the formation of needle-like crystals along the axis of fastest growth at high undercooling and a progressive tendency towards secondary nucleation on the interface of these needles so that spherulites are then formed. The development of needle-like growth at high undercooling, followed by spherulite formation associated with branching from these needle crystals at still higher undercooling, is indeed a ubiquitous phenomenon when crystallization occurs under conditions of high undercooling.^{112,113} This morphology is generic in bulk polymer materials, which have a high propensity for glass-formation because of the inherent complexity of their molecular structure. We can further anticipate impurities to have a very different influence on the dynamics of these different interfaces, offering a useful method for engineering material structure and properties.

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